ABSTRACT

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Atmospheric ammonia is a precursor to the formation of fine particulate matter, which contributes to human health problems and decreased visibility. Atmospheric ammonia may also be transported through wet and dry deposition to water bodies such as the Chesapeake Bay, contributing to excess nutrient loadings that cause eutrophication. Vehicle exhaust contains ammonia, created by a reaction of NO_x with H_2 in the three-way catalytic converter. Ammonia emissions were measured using a mass balance on the Fort McHenry Tunnel, Baltimore, Maryland. Atmospheric concentrations of gas-phase and particulate-phase ammonium were measured during 2003-2004 using denuders and filter packs. The average vehicle (veh) emission rate for these studies was 8.1 ± 4.3 mg NH_3-N veh^{-1} km^{-1}. We estimate the annual emission of ammonia from vehicles to be 151 metric tons NH_3-N yr^{-1} in Baltimore City and County and 707 metric tons NH_3-N yr^{-1} in all of Maryland.

VEHICULAR AMMONIA EMISSIONS IN BALTIMORE, MARYLAND

By

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Chapter 1: Introduction

The information presented in this thesis is the result of research done during the years 2003-2005 in the pursuit of a Master of Science degree in Marine, Estuarine and Environmental Sciences with a specialization in Environmental Chemistry at the University of Maryland, College Park. Laboratory work was done at the Chesapeake Biological Laboratory in Solomons Island, Maryland, a member laboratory of the University of Maryland Center of Environmental Sciences.

Three-way catalytic converters were introduced in 1975 to reduce the emissions of harmful chemicals such as carbon monoxide (CO), nitrogen monoxide (NO), nitrogen dioxide (NO_2), and unburned hydrocarbons from automobile exhaust. One side effect of the catalytic process is the reduction of NO_x (NO and NO_2) to ammonia (NH_3) via the reaction of nitrogen oxide with hydrogen on the catalyst (Equation 1) (Baum et al., 2001; Kean et al., 2000).

(1) $2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$

The amount of ammonia generated in this manner on the catalyst is dependent on vehicle operating conditions. Experiments show that vehicles operating fuel-rich exhibit higher ammonia emissions (Huai et al., 2000; Allen et al., 2001).

Ammonia is the primary basic gas in the atmosphere and can react with sulfuric and nitric acids (from sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions) to form secondary fine particulate matter with an aerodynamic diameter < 2.5 μm (PM2.5) in

the form of ammonium sulfate ($(NH_4)_2SO_4$), ammonium bisulfate (NH_4HSO_4), and ammonium nitrate (NH_4NO_3). PM2.5 is one of the six criteria pollutants designated by the Environmental Protection Agency (EPA) because of its adverse effect on human health and contribution to haze. In an effort to link air pollution to human health, a recent study conducted in Baltimore, Maryland, established a significant relationship between ambient PM2.5 measurements and human exposure samples (Landis et al., 2001). After it is inhaled, PM2.5 travels deeper into lung airways than larger particles and is retained in those airways (Churg & Brauer, 2000). An earlier study found that this fine particulate matter contributed to excess mortality in some U.S. cities (Dockery et al., 1993).

Particulate matter derived from atmospheric ammonia also contributes to haze and decreases visibility. A study conducted in the Baltimore-Washington region determined that ammonium sulfate comprised ~ 60% of the PM2.5 mass fraction during haze episodes (Chen et al., 2003), while a California study conducted near a dairy farming area with significant ammonia emissions found that ammonium nitrate was the largest component (Hughes et al., 2002).

Atmospheric ammonia may also cause problems in aquatic environments. Atmospheric nitrogen inputs (NO_3^- and NH_3) from sources such as chicken and hog livestock operations, agriculture, industry, and vehicle emissions have been found to account for between 24% (Castro & Driscoll, 2002) and ~ 35% (Howarth et al., 1996) of total nitrogen inputs to estuaries in the northeastern United States. These inputs are excess nutrients, causing eutrophication, which affects the health of aquatic flora

and fauna by causing algal blooms that block sunlight and create areas of low oxygen content.

This study measured vehicular ammonia emissions in the Baltimore, Maryland, metropolitan area to determine the significance of this source of ammonia to the region and Chesapeake Bay relative to other sources. It is part of a larger project assessing ammonia emissions and deposition from agricultural operations and urban areas in the Chesapeake Bay airshed. On-road vehicular ammonia emissions were measured in the Fort McHenry Tunnel, Baltimore, Maryland, on September 29, 2003, November 14, 2003, March 22, 2004, and June 10, 2004. Tunnels have been used effectively to measure vehicle emissions in a number of previous studies (Kean et al., 2000; Fraser et al., 1998; Moeckli et al., 1996; Pierson & Brachaczek, 1983), including in the Fort McHenry Tunnel (Pierson et al., 1996).

Chapter 2 of this thesis describes two pilot studies that were done prior to the main study to determine the most effective ammonia measurement method. Chapter 3 describes laboratory tests done in order to determine the effectiveness of the denuder coating solution that was used, as compared to other denuder coating solutions. Chapter 4 describes the main research project of this thesis, four field studies in the Fort McHenry Tunnel in Baltimore, MD. The collected data were analyzed, and an average ammonia emission rate determined. Chapter 5 describes work done with the Carnegie Mellon University Ammonia Model and presents results from executions of that model. Appendix A describes the analysis of error that was conducted. Appendix B discusses the velocity profile model used to determine mean air velocity in the tunnel.

Chapter 2: Fort McHenry Tunnel Pilot Studies

Introduction

In order to determine the best method for measuring atmospheric ammonia (NH_3) in the Fort McHenry Tunnel, Baltimore, Maryland, two pilot studies were conducted, one on July 29, 2003 and one on August 13, 2003. The first pilot study was conducted using Ogawa passive samplers deployed in such a way to calculate a vehicular emission rate in the tunnel. Because of their ease of use, and low cost, it was hoped that Ogawa passive samplers could be used to measure ammonia concentrations in the tunnel air. However, the lower than expected emission rate measured during the first pilot study caused concern that something was wrong with the sampling method. An additional concern with the samplers was that they only measure gas-phase ammonia. The second pilot study was conducted with Ogawa passive samplers and a glass annular denuder and filter pack combination placed side-by-side. Denuders deployed with filter packs are an apparatus know to sample ammonia effectively (Andersen & Hovmand, 1994). During the second pilot study, both types of samplers were deployed at the tunnel exit only, to provide ammonia air concentration measurements for comparison. No vehicular emission rate was calculated for the second deployment.

Methods

Sampling Site

A detailed description of the tunnel can be found in the Methods section of Chapter 4 of this thesis. The pilot study measurement locations were different than those used in the final study and are described in the following sections. One major measurement location difference was that ammonia measurements were taken at the tunnel bulkhead (Figure 2.1, location A), which divides the exhaust air shaft halfway along the tunnel length. The bulkhead was reached by walking from the tunnel exit through the exhaust air duct above the roadway.

Flow Rate Measurement

Anemometers, as described in Chapter 4, were used to measure air velocity. Air velocity measurements were corrected using the factor described in Chapter 4. For the first pilot study, air velocities were measured at the tunnel bulkhead and the tunnel exit by hanging the anemometer through vents in the ceiling (Figure 2.1, locations A & C), and in the fresh air duct at the tunnel exit (Figure 2.1, location D). For the second pilot study, air velocity was measured from the ceiling vents at the tunnel exit only.

Ammonia Measurement, Ogawa Passive Samplers

The Ogawa passive sampler is a Teflon cylinder consisting of two unconnected chambers. Each chamber holds a reactive filter, held in place with stainless steel screens. The ends of each chamber are capped off with a diffusion end cap containing 25 holes (Figure 2.2). The filters were impregnated with 100 μl of 2%

(w/v) citric acid-2% (v/v) glycerin in methanol. The samplers were kept frozen in airtight vials until deployment time and then deployed in a protective PVC cap, held in by a clip provided by the manufacturer. Samplers were always deployed three at a time to provide statistical replication, each within their own PVC protective cap (Figure 2.3). For deployment, the PVC caps were attached approximately 5cm apart to a metal rod.

In the first pilot study, 3-PVC cap/sampler assemblies were deployed at locations A, C, and D (Figure 2.1) for ~7 hours. The optimal deployment time of 7 hours for the passive samplers was determined using recent studies of vehicle ammonia emissions in conjunction with minimum exposure times determined by Roadman et al. (Roadman et al., 2003). The assemblies were hung through slits in the ceiling at locations A and C (Figure 2.1) with the closed part of the PVC caps facing traffic to protect the samplers. The assembly was mounted on a free-standing pole at location D (Figure 2.1).

In the second pilot study, two assemblies were deployed at the tunnel exit only (Figure 2.1, location C) and were left overnight for ~24 hours. One assembly was deployed with the closed caps facing traffic (perpendicular) and one with the caps aligned parallel to traffic to ensure that there was no problem with the orientation. Blanks were prepared and measured for each study and were kept in the airtight vials until extraction. Preparation and analysis of the Ogawa samplers for both pilot studies was done at the University of Delaware Graduate College of Marine Studies in Lewes, Delaware, according to the method detailed by Roadman et al. (Roadman et al., 2003).

Ammonia Measurement, Denuder/Filter Packs

A URG annual denuder and filter pack assembly was used to measure the ammonia concentration in the tunnel during the second pilot study. The preparation, operation, and extraction of the denuders and filter packs is described in Chapter 4 of this thesis, and in Figure 4.2, the only difference being that two denuders, instead of one, were deployed in series attached to the filter pack. The two denuders in series were deployed to ensure that the first denuder did not reach maximum ammonia trapping capacity. Denuder and filter extracts were analyzed using the OPA fluorescence method (Li et al., 1999). Analysis of the ammonia in the denuder and filter pack extracts was done at the Chesapeake Biological Laboratory and also at the University of Delaware.

Traffic Monitoring

Traffic was monitored for the first pilot study by videotaping the tunnel exit during the ammonia collection period from the control tower located at the north end of the tunnel. Vehicles were counted and classified as light or heavy-duty (diesel-burning). Vehicles were counted for the first ten minutes of each of the six video tapes. An average vehicle rate was calculated from these counts and used in the emission calculation.

Emission Calculation

The amount of ammonia produced per second (mg NH_3-N s^{-1}) in the portion of the bore sampled was calculated using a mass balance approach similar to the method detailed by Pierson et al. (Pierson et al., 1996) and described in detail in Chapter 4 of this thesis. An emission rate was not calculated for the second pilot study as

ammonia measurements were taken in only one location in order to compare the two methods.

Results and Discussion

Table 2.1 presents the air and ammonia measurements taken in the first pilot study. The emission rate was calculated from these measurements, the traffic counts, and the tunnel bulkhead to exit distance to be .67 mg NH_3-N veh^{-1} km^{-1}. This measurement was much lower than expected when compared to results of other vehicular ammonia emission studies (Table 4.6). Because of concern that the passive samplers were not measuring the ammonia concentration correctly, the second pilot study was conducted. Table 2.2 presents the results of the second pilot study. The ammonia concentration measured by the passive samplers was 8 μg NH_3-N m^{-3} and the concentration measured by the denuder/filter packs was 58 μg NH_3-N m^{-3} over the 24-hour period. Because of the low measurements reported by the passive samplers, it was decided that denuders and filter packs would be used in the final tunnel studies.

Two denuders were deployed in series in the second pilot study to ensure that the first denuder was not reaching capacity. The first denuder in series captured 818 μg NH_3-N while the second denuder captured 1.5 μg NH_3-N. Because the second denuder captured less than 1% of the total ammonia, it was assumed that the first denuder did not reach capacity and only one denuder was used going forward in the final tunnel studies.

Tables

Table 2.1 Pilot study ammonia concentrations, airflow rates, and mass flow rates at all measurement locations measured with Ogawa Passive Samplers in the Fort McHenry Tunnel, Baltimore, Maryland on July 29, 2003.

		Incoming Air		Outgoing Air	
Data	Field Blank	Air Entering With Vehicles (Location A)	West Ventilation Air (Location D)	Air Exiting With Vehicles (Location C)	Balance (Outgoing - Incoming)
Ammonia Concentration ($\mu g\ NH_3\text{-}N\ m^{-3}$)	1.7	2.8	0.7	3.7	N/A
Flow Rate ($m^3\ s^{-1}$)		332	45	339	-38
Mass Flow Rate ($mg\ NH_3\text{-}N\ s^{-1}$)		0.9	0.0	1.3	0.3

Table 2.2 Ammonia concentration measured by two different methods over a 24-hour period in the Fort McHenry Tunnel, Baltimore, Maryland, on August 14, 2003.

Method	Ammonia Concentration ($\mu g\ NH_3\text{-}N\ m^{-3}$)
Ogawa Passive Samplers	8
Denuder/Filter Packs	58

Figures

Figure 2.1 Pilot study airflow direction and sampling sites in the Fort McHenry Tunnel, Baltimore, Maryland.

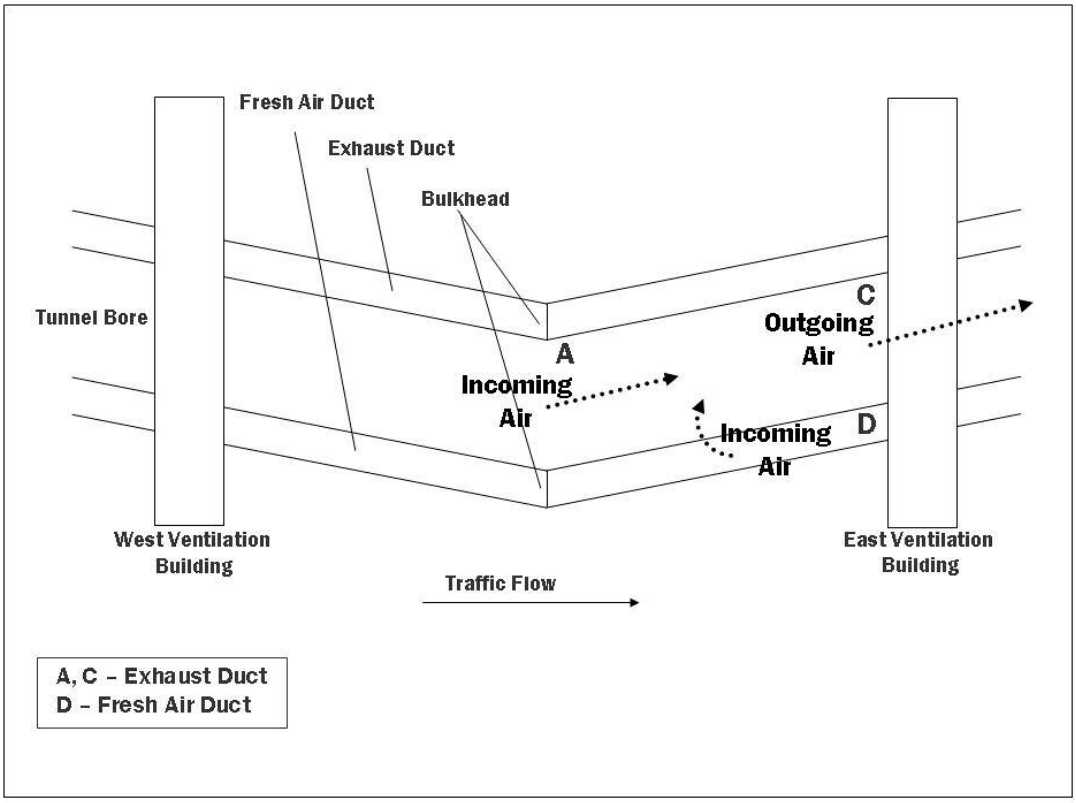


Figure 2.2 Ogawa passive sampler configuration. End cap (1), stainless steel screen (2), pre-coated collection filter (3), retainer ring (4), inner base pad (5), sampler body (6).

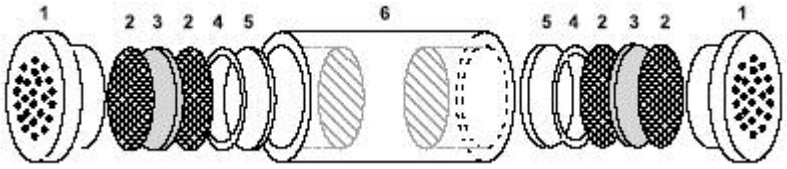


Figure 2.3 Ogawa passive sampler protective cap.

Chapter 3: Denuder Coating Verification

Introduction

Although the EPA method (EPA, 1999) and the URG website (www.urgcorp.com) suggest use of citric acid ($C_6H_8O_7$), oxalic acid ($H_2C_2O_4$), or phosphorus acid (H_3O_3P) as the denuder coating acid, other acidic coating solutions, such as phosphoric acid (H_3PO_4) have been used (Pisano & Fitz, 2002). The coating solution used in the final tunnel studies presented in this thesis (Chapter 4) was composed of 1% (v/v) phosphoric acid in 10% (v/v) methanol in DI water. To ensure that the phosphoric acid coating solution was as effective as those suggested by URG and the EPA, denuder/filter pack laboratory tests were done to compare the effectiveness of different coating solutions. Two denuder/filter pack laboratory tests were done to verify the coating solution on March 24, 2005, and on May 5, 2005. A phosphoric acid coating solution evaporation test was also conducted from September 1-3, 2004.

Methods

Denuder/Filter Pack Test

Citric acid, phosphoric acid, and phosphorus acid coating solutions were prepared. The citric acid solution was prepared by combining 0.5 g citric acid, 50 ml ethanol, and 0.5 ml glycerol. The phosphoric acid solution was prepared by combining 1 ml phosphoric acid, 10 ml methanol, and 90 ml DI water. The phosphorus acid solution was prepared by combining 1 g phosphorus acid, 90 ml methanol, and 10 ml DI water. Gas phase ammonia samples were collected using a URG annular denuder

(URG Corporation, URG-2000-30X242-3CSS, three channel, 242mm length), and particulate phase ammonium samples were collected with an attached URG 47mm filter pack (Figure 4.2) (Andersen & Hovmand, 1994). Each of the three coating solutions was used to prepare three denuders and filter packs following the method outlined in Chapter 4 of this thesis. The filter packs contained one Teflon filter and one prepared quartz filter. One of each of the three different acid-coated assemblies was used as a blank and the remaining six of the denuder/filter pack assemblies were mounted approximately 4 feet above the ground in the laboratory. A GAST vacuum pump regulated by a flow meter pulled air through each assembly at 10 L min^{-1}. Air traveled though the denuder/filter pack assembly first through an inlet cyclone with a 2.5 μm cutoff at 10 LPM, next through the annular denuder, and then through the filter pack (Figure 4.2). The airflow was adjusted to 10 ± 0.1 LPM through the assembly at the beginning of the deployment, checked 24 hours later, and checked at the end of the deployment period using a bubble flow meter (Gilibrator). Airflows at the end of the deployment were always within 3% of the initial reading and usually within 1%. The denuders/filter packs were left to sample for ~40 hours for the first deployment, and ~43 hours for the second.

At the end of the deployment time, the pumps were turned off and the denuders and filter packs were extracted according to the method described in Chapter 4 of this thesis. The Nutrient Analytical Services Laboratory at the Chesapeake Biological Laboratory analyzed samples from both tests using the Berthelot Reaction (Technicon, 1986).

An analysis of variance using an F-test ($\alpha = 0.05$) was done on the data from both days to determine if the mean ammonia concentrations found for each coating solution were statistically different from one another (Ott and Longnecker, 2001).

Evaporation Test

Phosphoric acid is a liquid at room temperature, while citric and phosphorus acid are solids. To ensure that phosphoric acid does not have the tendency to evaporate at room temperature, thus reducing its effectiveness at trapping ammonia, an evaporation test was conducted. 7.23 grams of phosphoric acid (a liquid) was placed in a glass petri dish about 4 inches in diameter. This amount of acid coated the bottom of the petri dish. The dish was then placed under an airflow from a 4-inch diameter hose with a face velocity of ~3.6 m s^{-1}. The petri dish was then weighed over a two day period to determine if any of the phosphoric acid had evaporated. The relative humidity in the area of the Petri dish ranged from 45 to 49% and the temperature was 73 °F.

Results and Discussion

The mass of NH_3 extracted from each of the samplers including the blanks is presented in Table 3.1. The mass of NH_3 extracted from the blank samplers was between 0 and 7% of the total extracted from the deployed samplers (Table 3.1). Concentration data from the denuder/filter pack tests is presented in Table 3.2. A statistical analysis of variance was done for each date. There was no statistically significant difference found between mean ammonia concentrations collected by each of the three coating solutions on either experiment date. This leads to the conclusion

that the three coating solutions are equally effective at trapping atmospheric ammonia. Although the citric acid and phosphorus acid solutions are suggested by the EPA and URG, the phosphoric acid coating solution used in the tunnel studies presented in this thesis is equally effective.

Data from the evaporation test is presented in Table 3.3. The results show that the phosphoric acid did not evaporate but actually is hygroscopic and takes up water from the air. This can be seen as the mass of the phosphoric acid actually increases over the time period of the experiment (Table 3.3). The results from this experiment lead to the conclusion that no evaporation of phosphoric acid occurs from the surface of the denuders or filters.

Tables

Table 3.1 Mass of ammonia extracted from samplers and blanks with three different coating solutions, citric, phosphoric, and phosphorus acid, on March 24 and May 5, 2005.

Date	Coating Solution	Ammonia Mass Extracted ($\mu g\ NH_3$)
24 Mar 2005	Citric Acid 1	24.4
	Citric Acid 2	36.4
	Citric Acid Blank	1.5
	Phosphoric Acid 1	30.7
	Phosphoric Acid 2	26.9
	Phosphoric Acid Blank	2.1
	Phosphorus Acid 1	30.2
	Phosphorus Acid 2	32.4
	Phosphorus Acid Blank	0.7
05 May 2005	Citric Acid 1	59.2
	Citric Acid 2	97.7
	Citric Acid Blank	0.3
	Phosphoric Acid 1	65.7
	Phosphoric Acid 2	63.7
	Phosphoric Acid Blank	0.2
	Phosphorus Acid 1	51.9
	Phosphorus Acid 2	65.4
	Phosphorus Acid Blank	0.7

Table 3.2 Mean ammonia concentrations captured by three different coating solutions, citric, phosphoric, and phosphorus acid, on March 24 and May 5, 2005.

Date	Coating Solution	Average Total Ammonia Concentration ($\mu g\ NH_3\text{-}N\ m^{-3}$)
24 Mar 2005	Citric Acid	1.2 a*
	Phosphoric Acid	1.2 a
	Phosphorus Acid	1.3 a
05 May 2005	Citric Acid	3.1 b
	Phosphoric Acid	2.5 b
	Phosphorus Acid	2.3 b

* Means with different letters indicate significant differences, $\alpha = 0.05$.

Table 3.3 Results of phosphoric acid (H_3PO_4) evaporation test conducted from September 1-3, 2004.

Date	Time	Mass (g H_3PO_4)
01 Sep 2004	12:22	7.23
	12:40	8.03
	12:46	8.22
	13:07	8.66
	13:16	8.85
	13:22	8.93
	13:25	8.98
	15:32	9.64
	15:53	9.67
	16:33	9.75
02 Sep 2004	8:28	10.10
	9:18	10.04
	12:29	9.92
	16:39	9.94
03 Sep 2004	10:34	10.07

Chapter 4: Fort McHenry Tunnel Studies

Introduction

To determine an on-road ammonia emission rate for the Baltimore fleet, this study measured on-road vehicular ammonia emissions in the Fort McHenry Tunnel, Baltimore, Maryland, on September 29, 2003, November 14, 2003, March 22, 2004, and June 10, 2004. Acid-coated denuders and filter packs were used to capture ammonia, and anemometers were used to measure air velocity in the tunnel.

Methods

Sampling Site

Vehicular ammonia emissions were measured during four separate field studies at the Fort McHenry Tunnel in Baltimore, Maryland. The 2.2 km long tunnel carries traffic under the Baltimore Harbor on Interstate 95 through four bores that contain two lanes of traffic each. Heavy-duty (HD) vehicles are directed to the exterior bores in both directions, while light-duty (LD) vehicles travel through both the interior and exterior bores during normal tunnel operations. HD vehicles are defined as diesel-fuel burning trucks and LD vehicles as gasoline-burning. It is not mandatory for HD vehicles to use the exterior bores and therefore there is still a mix of LD and HD vehicles that enter the interior bores. LD vehicles equipped with three-way catalytic converters emit more ammonia than vehicles without catalytic converters (Der, 1999; Fraser & Cass, 1998; Pierson et al., 1996; Cadle & Mulawa, 1980), therefore bore three, the interior northbound traffic bore, which was expected to contain a large

fraction of LD vehicles, was used as the main sampling site to maximize ammonia concentration in the tunnel. Bore three was used for each field deployment except for the last deployment. Bore three was closed on the day of the last deployment so all traffic was diverted to bore four and measurements were made there.

A fresh air ventilation duct runs the length of each bore below the roadbed, and an exhaust duct runs the length of each bore above the roadbed (Figure 4.1). Most of the outside air entering the tunnel is pushed by the traffic through the tunnel entrance by the "piston effect" (Pierson et al., 1996). Fresh air also enters the tunnel through forced ventilation along most of the tunnel length through fresh air ventilation ducts just above the roadbed along the sides of the tunnel. Exhaust air leaves the tunnel, pushed by the traffic, through the tunnel exit. Air from the tunnel can also be removed by fans through an exhaust ventilation system above the tunnel. However the fan exhaust system is used primarily for emergencies and was never used during this study.

Flow Rate Measurement

Air velocities were measured using Extech Model 451126 Van Thermo-Anemometer Dataloggers at 10-second intervals over the duration of each deployment. The air velocity measurements were collected in the tunnel by hanging the anemometers through vents in the ceiling of the tunnel at locations A and C (Figure 4.1). The anemometers hung suspended 0.25 m from the ceiling. The velocity profile in the tunnel was calculated by approximating the tunnel as a circular pipe and using the equations for turbulent flow (Green & Maloney, 1997). The velocity profile has a very sharp gradient near the wall because of the turbulent flow (Figure B.1). The

velocity at 0.25 m from the tunnel walls was ~ 6% lower than the mean tunnel velocity at the tunnel entrance, and ~4.3% lower at the tunnel exit (Table B.1). The anemometer measurements at locations A and C (Figure 4.1) were adjusted by these factors to account for the velocity profile. See Appendix B for a more detailed description of the velocity profile and corrections. Incoming air velocity measurements were collected in the fresh air ventilation ducts below the entrance and exit of the bore (Figure 4.1, locations B and D). These anemometers stood in the center of the duct and no corrections were made to account for the velocity profile since these flows usually represented < 10% of the total flow into the bore. The velocity measurements were averaged for each location and converted to airflow by multiplying the velocity by the cross-sectional area at the measurement locations.

Ammonia Measurement

The incoming ammonia air concentration was measured at the tunnel entrance (Figure 4.1, location A) and in the fan room that supplies ambient air to the fresh air ventilation ducts (Figure 4.1, location E). The ambient air measurement in the fan room was extrapolated to the fresh air duct locations (Figure 4.1, locations B and D) for the mass balance calculation. The outgoing ammonia air concentration was measured at the tunnel exit (Figure 4.1, location C). The incoming and outgoing ammonia air concentrations were measured by placing the sampling inlets through the ventilation slits in the exhaust duct floor (i.e., the roadbed ceiling). The entrance and exit sampling locations were approximately fifty meters from the tunnel openings because of safety and accessibility to these locations. One coated denuder/filter pack set was transported to the sampling site to be used as a field blank and not deployed.

Gas phase ammonia samples were collected using a URG annular denuder (URG Corporation, URG-2000-30X242-3CSS, three channel, 242mm length), and particulate phase ammonium samples were collected with an attached URG 47mm filter pack (Figure 4.2) (Andersen & Hovmand, 1994). A GAST vacuum pump regulated by a flow meter pulled air through the assembly at 10 L min^{-1}. Timers attached to the vacuum pumps at each sampling location were used to synchronize the start and stop of airflow through the denuders and filter packs. Air traveled though the denuder/filter pack assembly first through an inlet cyclone with a 2.5 μm cutoff at 10 LPM, next through the annular denuder, and then through the filter pack (Figure 4.2). The airflow was adjusted to 10 ± 0.1 LPM through the assembly at the beginning of the deployment and checked at the end of the deployment period using a bubble flow meter (Gilibrator). Airflows at the end of the deployment were always within 7% of the initial reading and usually within 2%.

Annular denuders were coated with a 1% (v/v) phosphoric acid (H_3PO_4)-10% (v/v) methanol in DI water solution and then dried in a laminar flow hood with a pre-filter coated with the same solution to minimize ammonia contamination during the drying process. Phosphoric acid was used in this study since it has been shown effective in other experiments (Pisano & Fitz, 2002), although other acidic coatings are more common (e.g., the EPA method suggests the use of oxalic acid as a coating medium (EPA, 1999)). A 47mm Zefluor 2.0 μm filter was placed first in the filter pack to collect particulate matter, followed by a 47mm Nylasorb 1.0 μm filter to collect volatilized HNO_3 from the Zefluor filter, and finally a 47mm Whatman quartz fiber filter to collect volatilized NH_3 from the Zefluor filter. The quartz fiber filter was

coated with a 1% H_3PO_4 solution and dried in a laminar flow hood with a pre-filter coated with the same solution to minimize ammonia contamination.

The extraction of the denuders and filters was based on the EPA Method, "Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles <2.5 μm" (EPA, 1999). The denuders were extracted using three rinses of 10 ml of DI water each. The quartz fiber filters were extracted by immersing the filters in DI water and then sonicating them for 15 minutes. The extraction solution was filtered through a Gelman Ion Chromatography Acrodisc 0.45 μm filter to remove dislodged quartz fibers. The Zefluor filters were extracted by wetting the surface with approximately 150 μl of ethanol, immersing the filter in DI water, and then sonicating for 15 minutes. All of the filters were extracted twice and each extraction solution was analyzed separately. Analysis of the samples from the fourth deployment included extraction of the cyclones and the inlet tubes with two 10 ml washes of DI water each. These additional extractions were done to investigate the quantity of ammonium particles captured on the walls of the cyclone and inlet tubes.

Extracted samples from the first deployment were analyzed at Chesapeake Biological Laboratory (CBL) using ion chromatography (IC) on a Dionex DX-600 system. A CS12A cation column (Dionex) with a methanesulfonic acid (MSA) eluent in gradient mode separated and eluted the cations. The samples from the second and third deployments were analyzed at CBL using the OPA fluorescence method (Li et al., 1999). Standards were prepared for both of these methods by diluting the Ultra

Scientific Ammonium 1000 μg ml^{-1} standard. If necessary, samples were diluted with DI water to bring the concentrations within the calibration range. The Nutrient Analytical Services Laboratory at the Chesapeake Biological Laboratory analyzed samples from the fourth deployment using the Berthelot Reaction (Technicon, 1986). The three methods have a similar error rate, in the range of ± 10%. Quality is assured for the IC and OPA methods in the CBL laboratory by using the same ammonium standards to calibrate the instruments, and by lab participation in the Chesapeake Bay Blind Audit Program. Quality assurance procedures for the Berthelot Reaction performed in the CBL Nutrient Analytical Services Laboratory are documented on their website (http://www.cbl.umces.edu/nasl/index.htm).

Traffic Monitoring

Traffic was monitored by videotaping the tunnel exit during the ammonia collection period from the control tower located at the north end of the tunnel. Vehicles were counted and classified as light or heavy-duty.

Emission Calculation

The amount of ammonia produced per second (mg NH_3-N s^{-1}) in the portion of the bore sampled was calculated using a mass balance approach similar to the method detailed by Pierson et al. (Pierson et al., 1996):

$$M = \sum_i (C_{out} V_{out})_i - \sum_j (C_{in} V_{in})_j$$

Where $(C_{out} V_{out})_i$ is the product of the concentration of ammonia in the air exiting the tunnel (mg NH_3-N m^{-3}) and the volumetric flow rate of air exiting the

tunnel (m^3s^{-1}), and $\left(C_{in}V_{in}\right)_j$ is the product of the concentration of ammonia in the air entering the tunnel and the volumetric flow rate of air entering the tunnel. Ideally V_{out} is equal to V_{in} if all of the incoming and outgoing air has been accounted for. In the Fort McHenry Tunnel, air exits through only one location, therefore i = 1, while air enters through three locations (tunnel entrance, and entrance and exit fresh air ventilation ducts), therefore j=3 and the above product for incoming air was summed for these locations. The mass flow rate of ammonia produced in the section of the bore sampled (M, mg NH_3-N s^{-1}) was calculated by subtracting the sum of the incoming products from the outgoing product. Field blank measurements were subtracted from each tunnel measurement prior to the mass balance calculation. The vehicular (veh) ammonia emission rate was calculated by dividing the amount of ammonia generated per second (M, mg NH_3-N s^{-1}) by the total number of vehicles per second (V, veh s^{-1}), and then by the length of the tunnel in kilometers (L, km), i.e.,

$$E = M / (VL).$$

The estimate of error was calculated for each deployment using a ±10% error for the ammonia measurement device and the estimated error for each other measurement used in the mass balance calculation. The uncertainties were propagated through the emission rate calculation to determine the overall emission rate error estimate (Appendix A).

Results and Discussion

Emission Rates

In order for the mass balance method of calculating ammonia emissions in the tunnel to be accurate, the volumetric airflow rate of the incoming air must balance that of the outgoing air. Airflow rate was calculated using the average velocity at each location (Table 4.1). Velocity was highly variable at each location which can be seen in an example from the deployment on November 14, 2003 (Figure 4.3). Although no velocity data from other studies is available for the Fort McHenry tunnel, Pierson et al., found a tailwind speed of 5.3 m s^{-1} in the Tuscarora Mountain Tunnel which is similar in length and traffic speed to the Fort McHenry Tunnel (Pierson et al, 1996). The similarity between 5.3 m s^{-1} and the corrected entrance tunnel velocities measured in this study, which were between 4.74 and 5.78 m s^{-1} (Table 4.1), adds confidence to our measurements. A discussion of the velocity profile model used and velocity correction factors can be found in Appendix B. Table 4.2 lists the incoming and outgoing air volumetric flow rates measured for each deployment. The flow balance shows reasonable agreement for each of the deployments with the outgoing air balancing the incoming air within 10% or less for all of the deployments. This agreement provides confidence that the airflow measurements were accurate.

The ammonium concentration extracted from the samplers at each sampling location including the blank samplers is presented in Table 4.3. The blank concentrations ranged between 0 and 11% of the concentration extracted from samplers of the corresponding date (Table 4.3). The ammonia concentration measured at each

sampling location for each deployment is presented in Table 4.4. The ammonia concentration measurements in Table 4.4 are totals, including both gaseous ammonia and particulate ammonium. Table 4.4 also lists the calculated mass flow rate of ammonia for each location and the calculated ammonia mass balance for each deployment in units of mass of ammonia generated per second (mg NH_3-N s^{-1}). The ammonia mass flow rates ranged between 2.3 and 12.0 mg NH_3-N s^{-1} for the four deployments.

Table 4.5 presents the ammonia emission rates determined in this experiment. The average emission rate measured was 8.1 ± 4.3 mg NH_3-N veh^{-1} km^{-1}. Emission rates of gas-phase, particulate-phase, and total are presented separately in Table 4.5. The particulate-phase emission was between 0% and 5% of the total for deployments one, three and four, however, it was 74% of the total for deployment two. An estimate of particulate-phase ammonium lost to the denuder inlet tube and cyclone chamber walls was determined during the fourth deployment. Analysis of inlet tube and cyclone extractions for each denuder resulted in an average of 17% of the total particulate ammonium lost to these components. Using the 17% correction to update concentrations from the prior deployments resulted in a < 1% change to the overall mass balance for deployments one and three because of the small particulate emissions measured in these deployments. Applying the correction to the emission rate measured in deployment two makes a significant difference in the emission rate because of the high particulate matter emission measured in that deployment. However the correction was not applied to any of the deployments because of the uncertainty in the amount of the correction. Further experiments should be

undertaken to determine the exact emission rate correction to be made from particulate matter loss to the cyclone and inlet tube.

The cyclone of the denuder apparatus excludes particulate matter with aerodynamic diameters > 2.5 μm. If ammonia emissions in the tunnel were present in significant amounts on particulate matter > 2.5 μm, the emission estimate would be under-predicted. To ensure that this was not the case, open face filter packs with no aerodynamic diameter exclusion limit were deployed without denuders next to the denuder and filter pack combinations in the fourth deployment. The total ammonia concentration that was calculated for the filter pack alone was between 2% and 7% different when compared to the denuder and filter pack combination, leading to the conclusion that no significant amounts of particulate ammonium were excluded, and that the denuders were equally as efficient as the coated filters at collecting gas-phase ammonia.

The traffic rate for each deployment is also presented in Table 4.5. Traffic moved at similar speeds and similar volumes for all four deployments. The average proportion of HD vehicles for the first three deployments was 3-4% of the total number of vehicles going through the tunnel. The fourth deployment was conducted in the exterior northbound bore, into which HD vehicles were directed by tunnel protocol. As expected, the percentage of HD vehicles was greater for the fourth deployment, at 25%. A greater percentage of HD vehicles is expected to cause the emission rate to be lower per vehicle because HD vehicles without catalytic converters are known to emit less ammonia (Der, 1999; Fraser & Cass, 1998; Pierson et al., 1996; Cadle &

Mulawa, 1980). The emission rate for deployment four is lower than deployments one and two, as expected, although still greater than deployment three. It is possible to correct the emission rates by accounting for LD vehicle miles only. When this correction is made, the emission rate for the fourth deployment becomes 10.7 ± 3.4 mg NH_3-N veh^{-1} km^{-1}, which is closer in value to the corrected emission rates from deployments one and two (Table 4.5). The corrected emission rates represent the ammonia emission rate for LD vehicles.

The emission rates for deployments one, two, and four are similar in magnitude. However, the emission rate for deployment three is ~ 70% less than the average of the other three deployments. The lowest ambient temperature, and the lowest relative humidity occurred on the day of deployment three (Table 4.5). More investigation is necessary to determine if temperature and relative humidity have an effect on the vehicular emissions reaching the sampling equipment.

Comparison to Previous Studies

Other studies have investigated vehicular ammonia emissions and are presented in Table 4.6. It should be noted that the average ammonia emission rate measured in our study, 8.1 ± 4.3 mg NH_3-N veh^{-1} km^{-1}, is lower than those calculated in two recent, similar studies. Kean et al. determined an emission rate of 40 mg NH_3-N veh^{-1} km^{-1} in San Francisco in 1999 (Kean at al., 2000), and Fraser and Cass calculated an emission rate of 50 mg NH_3-N veh^{-1} km^{-1} in Los Angeles in 1993 (Fraser & Cass, 1998). Moeckli et al. measured an emission rate of 12 mg NH_3-N veh^{-1} km^{-1} in Zurich, Switzerland, in 1995 (Moeckli et al., 1996), a rate much closer to those measured in this study. In 1981, Pierson and Brachaczek measured a rate of 1.1 mg

NH_3-N veh^{-1} km^{-1} (Pierson & Brachaczek, 1983), which is much lower than this study and other recent studies. In 1981 the percentage of vehicles on the road with three-way catalytic converters was much lower than it is today, although catalytic converters were made mandatory in 1975. Other studies have also measured vehicular ammonia emissions without the use of a tunnel. Baum et al. determined an emission rate of 78 mg NH_3-N veh^{-1} km^{-1} using a remote sensing technique in 1999 (Baum et al., 2001), and Durbin et al. used chassis dynamometer test cycles to determine an emission rate of 28 mg NH_3-N veh^{-1} km^{-1} in 2001 for a test set of LD vehicles only (Durbin et al., 2002). The Durbin study used the FTP test cycle which simulates an urban route with frequent stops, and the US06 cycle which simulates high acceleration, aggressive highway driving (http://www.epa.gov/oms/labda.htm#vehcycles). Neither of these test cycles are similar to the driving conditions seen in the Fort McHenry Tunnel. Vehicle ammonia emission measurements published thus far are varied, which makes choosing a rate for modeling traffic emissions a difficult task.

Vehicular Ammonia Emission Impact

According to the 2003 "Millions of Annual Vehicle Miles" report from the Maryland Department of Transportation (MDOT, 2003), 1.9×10^{10} kilometers were driven in Baltimore City and Baltimore County in 2003 and 8.8×10^{10} kilometers were driven in all of Maryland. Using our emission rates, these kilometers driven translate into a total emission of 151 mtpa (metric tons per annum) NH_3-N in Baltimore City and County and 707 mtpa NH_3-N in all of Maryland.

The Carnegie Mellon University Ammonia Model (CMU Model) (Davidson et al., 2001) provides monthly ammonia emissions by county for the United States. The emissions are classified into the following source categories: livestock, fertilizer, soil, mobile, industry, domestic animals, wild animals, and miscellaneous. After the model was updated to use the emission rates determined in this study (Chapter 5), the CMU Model predicts annual emissions from mobile sources of 121 mtpa NH_3-N for Baltimore City and County and 520 mtpa NH_3-N for all of Maryland (Table 5.1). These estimates are very similar to our predictions and any differences probably arise from traffic data. The model predicts total ammonia emissions from all sources to be 2,730 mtpa NH_3N in Baltimore City and County, and 37,776 mtpa NH_3-N in the state of Maryland (Table 5.1). Of the Maryland total, 50% is from agriculture (livestock and fertilizer sources) while only 1% is from mobile sources (Figure 5.1). Looking at Baltimore City and Baltimore County together, a more urban area, mobile sources contribute 4% of the total NH_3-N emission (Table 5.2).

Another source comparison is provided by a recent study of ammonia emissions from chicken houses on the Eastern Shore of Maryland (Siefert et al., 2004). The chicken houses are estimated to emit 18,000 mtpa NH_3-N. This estimate is ~ 48% of the total emissions predicted for all of Maryland by the CMU Model, and much larger than vehicular ammonia emission predictions.

It is difficult to determine vehicular impact on total ammonia emissions, as mobile emission factors vary from source to source. Vehicular ammonia emission is probably not a large contributing factor of atmospheric ammonia to the Chesapeake Bay compared to other regional sources. However, within populated areas, such as

Baltimore City, vehicular ammonia emissions are still an important contributing factor to visibility and health problems via formation of PM2.5.

Tables

Table 4.1 Average air velocity measured at each sampling location in the Fort McHenry Tunnel, Baltimore, Maryland, on four sampling dates.

	Incoming Air (m s^{-1})			Outgoing Air (m s^{-1})
Sampling Date	Air Entering with Vehicles (Location A)	West Ventilation Air (Location B)	East Ventilation Air (Location D)	Air Exiting With Vehicles (Location C)
29 Sep 2003	4.74	2.83	2.80	5.36
14 Nov 2003	5.48	2.72	2.82	6.73
22 Mar 2004	5.22	2.44	3.98	6.03
10 Jun 2004	5.78	1.86	3.99	6.50

Table 4.2 Volumetric airflow balance measured in the Fort McHenry Tunnel, Baltimore, Maryland, on four sampling dates.

	Incoming Air ($m^3 s^{-1}$)				Outgoing Air ($m^3 s^{-1}$)	Flow Balance ($m^3 s^{-1}$)
Sampling Date	Air Entering with Vehicles (Location A)	West Ventilation Air (Location B)	East Ventilation Air (Location D)	Total Incoming	Air Exiting With Vehicles (Location C)	Outgoing - Incoming
29 Sep 2003	259	36	35	331	293	-37
14 Nov 2003	300	35	36	370	368	-2
22 Mar 2004	285	31	51	367	330	-37
10 Jun 2004	316	24	51	391	356	-35

Table 4.3 Extracted ammonium concentrations for samplers at all sampling sites including blanks measured in the Fort McHenry Tunnel, Baltimore, Maryland, on four sampling dates.

	Extracted Ammonium Concentration (μM)			
Sampling Date	Blank	Air Entering with Vehicles (Location A)	Fresh Air Fan Room (Location E)	Air Exiting With Vehicles (Location C)
29 Sep 2003	0.16	3.52	1.40	9.82
14 Nov 2003	0.05	0.88	1.07	5.14
22 Mar 2004	0.00	0.61	0.03	1.46
10 Jun 2004	0.09	1.98	1.29	4.84

Table 4.4 Values of ammonia (± estimate of error) in incoming and outgoing air measured in the Fort McHenry Tunnel, Baltimore, Maryland, on four sampling dates presented as concentration and mass flow rates. A - Air entering with vehicles, B - West ventilation air, D - East ventilation air, C - Air exiting with vehicles (Figure 4.1). Mass balance of ammonia generated (± estimate of error) is calculated as mass flow rates C - (A + B + D).

	Concentration ($\mu g\ NH_3\text{-}N\ m^{-3}$)				Mass Flow Rate ($mg\ NH_3\text{-}N\ s^{-1}$)				
	Incoming			Outgoing	Incoming			Outgoing	Mass Balance
Sampling Date	A	B	D	C	A	B	D	C	Ammonia Generated
29 Sep 2003	12.4 ± 1.2	6.1 ± 0.5	6.1 ± 0.5	47.2 ± 4.7	3.2 ± 0.6	0.2 ± 0.0	0.2 ± 0.0	13.8 ± 2.2	10.2 ± 2.3
14 Nov 2003	6.5 ± 0.6	7.9 ± 0.7	7.9 ± 0.7	39.3 ± 2.7	1.9 ± 0.4	0.3 ± 0.1	0.3 ± 0.1	14.5 ± 2.5	12.0 ± 2.5
22 Mar 2004	4.7 ± 0.5	0.2 ± 0.0	0.2 ± 0.0	11.2 ± 1.1	1.3 ± 0.3	0.0 ± 0.0	0.0 ± 0.0	3.7 ± 0.7	2.3 ± 0.7
10 Jun 2004	12.7 ± 1.1	8.5 ± 0.7	8.5 ± 0.7	32.7 ± 2.9	4.0 ± 0.7	0.2 ± 0.0	0.4 ± 0.1	11.6 ± 2.1	7.0 ± 2.2

Table 4.5 Ammonia emission rates (± estimate of error) and other data measured in the Fort McHenry Tunnel, Baltimore, Maryland, on four sampling dates.

	Emission Rate (mg NH_3-N veh^{-1} km^{-1})*								
Sampling Date	Gas-Phase Only	Particulate-Phase Only	Total	Corrected Rate (Light-Duty Only)	Method**	Vehicle Rate (veh min^{-1})	Percent Heavy-Duty Vehicles	Ambient Temperature (°C)	Ambient Relative Humidity (%)
29 Sep 2003	10.2 ± 2.2	0.0 ± 0.1	10.2 ± 2.3	10.5 ± 2.4	IC	31	3%	13	69
14 Nov 2003	3.0 ± 1.0	8.4 ± 1.6	11.4 ± 2.4	12.1 ± 2.6	OPA	33	4%	5	45
22 Mar 2004	2.7 ± 0.9	0.1 ± 0.0	2.8 ± 0.9	2.9 ± 0.9	OPA	26	3%	0	40
10 Jun 2004	7.5 ± 2.3	0.4 ± 0.3	7.9 ± 2.5	10.7 ± 3.4	Berthelot	28	25%	26	70
Average			8.1 ± 4.3	9.0 ± 5.0					

* veh = vehicle.

** Methods described in detail in Chapter 4.

Table 4.6 Values of vehicular ammonia emission rates from seven studies.

Year	Researchers	Emission Rate (mg NH_3-N veh^{-1} km^{-1})*
Tunnel Studies		
1981	Pierson and Brachaczek (13)	1
1993	Fraser and Cass (11)	50
1995	Moeckli, Fierz, and Sigrist (12)	12
1999	Kean and Harley (2)	40
2004	Erwin and Siefert	8
Other Studies		
1999	Baum, Kiyomiya, Kumar, and Lappas (1)	77
2001	Durbin, Wilson, Norbeck, Miller, Huai, and Rhee (22)	28**

* veh = vehicle

** Light-duty vehicles only

Figures

Figure 4.1 Airflow direction and sampling sites in the Fort McHenry Tunnel, Baltimore, Maryland.

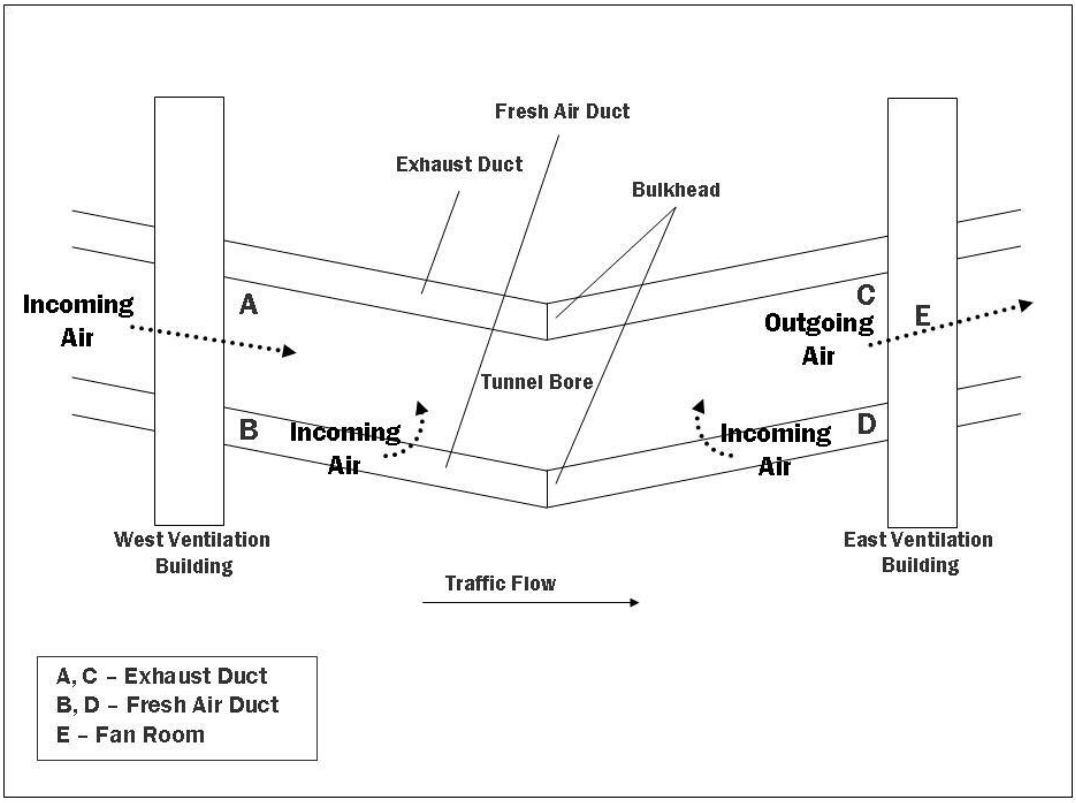


Figure 4.2 Denuder and filter pack assembly.

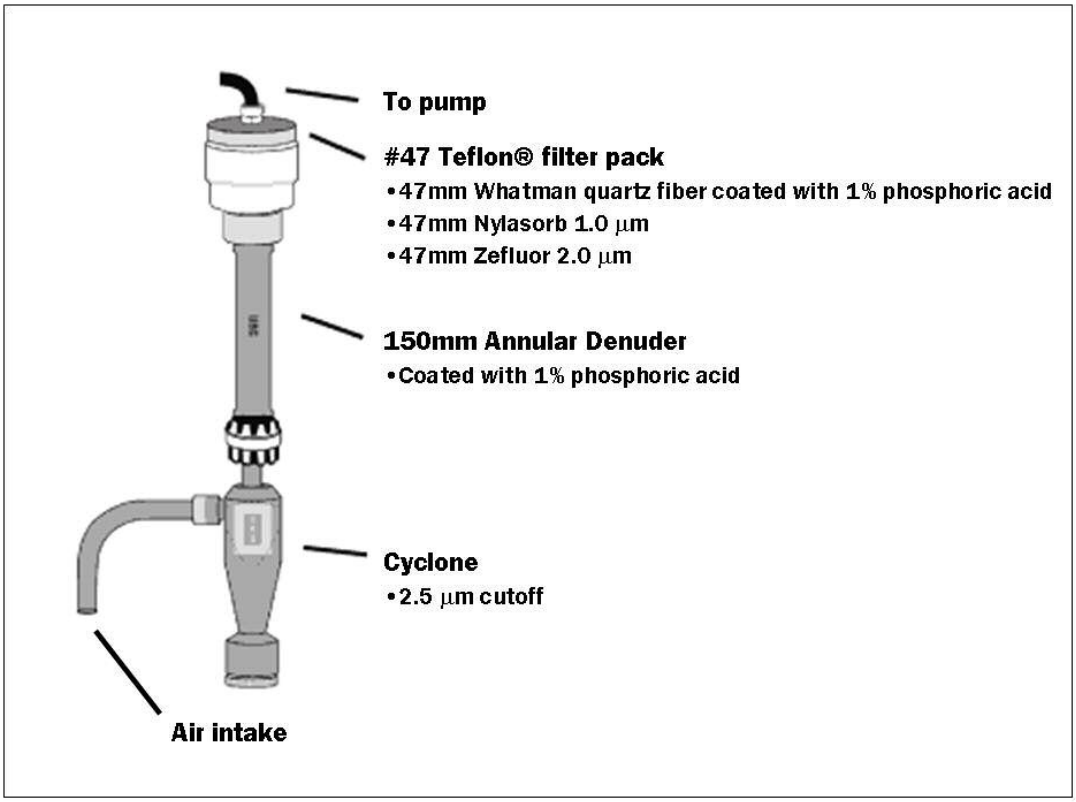
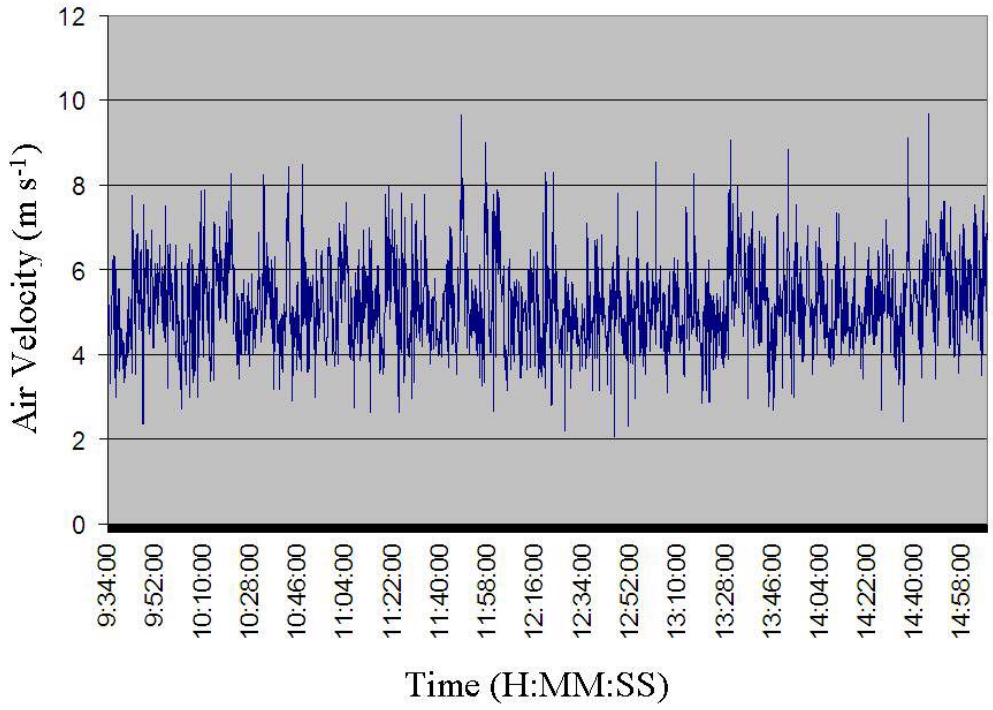


Figure 4.3 Velocity vs. time graph for deployment on November 14, 2003 in the Fort McHenry Tunnel, Baltimore, Maryland.



Chapter 5: Carnegie Mellon University Ammonia Model

Introduction

The goal of the research presented in this thesis was to determine an ammonia emission rate for vehicles of the Baltimore fleet. The emission rate determined in this study was then compared to ammonia emission rates from other sources in the area to determine its relative importance. The Carnegie Mellon University Ammonia Model (CMU Model) was used to determine the ammonia emissions from other sources as well as to model mobile emissions for Maryland.

The CMU Model was developed by Cliff Davidson and a team of researchers at Carnegie Mellon University in 2001 for the Northeast States for Coordinated Air Use Management (NESCAUM), and the Mid-Atlantic Regional Air Management Association (MARAMA) (Davidson et al., 2001). The model can be downloaded at www.cmu.edu/ammonia. The model provides an estimate of monthly ammonia emissions in the United States at a county level for a number of different sources including livestock, fertilizer, soil, mobile sources, industry, publicly owned treatment works, humans, domestic animals, wild animals, and biomass burning. The model is very flexible and the user can easily change factors as new research is published. Emission rates output by the model are in kg NH_3 yr^{-1} or kg NH_3 $month^{-1}$, which were converted to mtpa NH_3 (metric tons NH_3 per year) for presentation in this thesis.

Ammonia Emission Factors and Activity Levels

Emission factors and activity levels incorporated by the model in 2001 were gathered from a number of different sources as described below (Davidson, 2001). An emission factor is the amount of ammonia produced monthly in each county by a source unit. A source unit may be a cow, a human, a type of soil, or a car, for example. Emission activity level is the number of units per county per month. These two inputs are used to calculate ammonia emissions by county, by month. Factor and activity updates have been made to the model since its inception and are included in version 3, the most recent version.

Mobile Sources

The mobile source emission rates used in the CMU Model were initially taken from a study done by Battye et al. for the EPA (Battye et al., 1994) and then updated based on the STi report (Chinkin et al., 2003). The CMU Model, version 3, uses an emission rate of 60.6 mg NH_3-N km^{-1} for LD vehicles, which is much greater than the rate measured in this study. It uses a rate of 17 mg NH_3-N km^{-1} for HD vehicles, which is inconsistent with the fact that HD vehicles emit much less ammonia than catalytic converter equipped automobiles (Der, 1999; Fraser & Cass, 1998; Pierson et al., 1996; Cadle & Mulawa, 1980). The emission factor used to calculate emissions for LD mobile sources in the CMU Model was updated to 8.1 mg NH_3-N veh^{-1} km^{-1} to reflect the results of this study, and the factor used to calculate emissions for heavy-duty mobile sources was updated to 0 mg NH_3-N veh^{-1} km^{-1}. Mobile source activity levels for each county were gathered from state transportation departments.

Other Sources

Livestock	Activity levels from USDA data for 1992, and 1997. Composite emission factors for each USDA livestock category from Battye et al., 1994.
Fertilizer	Activity levels from Association of American Plant and Food Control Officials. Emission factors from Battye et al., 1994 and Asman et al., 1992. Monthly distribution determined from USDA data.
Soil	Activity levels from Anderson land use codes. Emission factors from Cass et al., 1982. This is the most uncertain of all the source categories.
Industry	Actual ammonia emissions for industry from the EPA Toxic Release Inventory (TRI) database. These values are highly uncertain.
Domestic Animals	Category includes cats and dogs. Activity levels from the American Veterinary Medical Association. Emission factors form Battye et al., 1994.
Wild Animals	Category includes bear, deer, and elk. Activity levels from Rocky Mountain Elk Foundation, American Bear Association, and the Quality Deer Management Association. Emission factors determined by Botsford in 1997.

Miscellaneous Category includes Publicly Owned Treatment Works (POTWs), humans, and wildfires. POTW activity levels from the EPA Office of Water. POTW emission factors from Battye et al., 1994. Human activity levels from the US Census, and emission factors (from breath and perspiration) from Battye et al, 1994. Wildfire activity levels from the National Interagency Fire Center. Wildfire emission factors computed by combining an emission factor of CO from wildfires provided by the EPA with a ratio of NH_3/CO measured by Hegg in 1998.

Model Execution Results

The CMU Model predicts annual emissions from mobile sources of 121 mtpa NH_3-N for Baltimore City and County and 520 mtpa NH_3-N for all of Maryland (Table 5.1). These estimates are very similar to our predictions and any differences probably arise from traffic data. The model predicts total ammonia emissions from all sources to be 2,730 mtpa NH_3-N in Baltimore City and County, and 37,776 mtpa NH_3-N in the state of Maryland (Table 5.1).

The model was executed for all counties in Maryland to provide ammonia emissions for the entire state. Baltimore County and Baltimore City data were separated to show relative source ammonia emission data for a largely urban area. Figure 5.1 presents relative ammonia emissions by source for the state of Maryland. The greatest contributors of ammonia emissions statewide are livestock and soil, while

mobile sources contribute only 1% of the total ammonia emitted. Figure 5.2 presents relative ammonia emissions by source for Baltimore City and Baltimore County. Because these two areas contain major urban areas, mobile sources are a greater contributor. Mobile sources contribute 4% of the total emissions while livestock drops to 6%. Soil and domestic animal emissions are important contributors at 29% each.

Figure 5.3 presents total ammonia emissions by county for the state of Maryland. The counties exhibiting the highest ammonia emissions probably do so because of large agricultural areas. Figure 5.4 presents mobile ammonia emissions by county for the state of Maryland. As expected, the more urban counties surrounding Baltimore, MD and Washington, DC (Baltimore County, Baltimore City, Anne Arundel County, Prince George's County, Howard County, and Montgomery County) show greater mobile ammonia emissions.

According to the mobile ammonia emission rate calculated in this thesis and results of the CMU Model, mobile emissions are not a relatively important contributor, although they are more important in urban areas.

More work should be done to better quantify all ammonia source data for Maryland to update the CMU Model.

Tables

Table 5.1 Annual ammonia emission estimates calculated using thesis data and CMU Model output.

	Thesis Prediction (mtpa NH_3-N)*	CMU Model Prediction (mtpa NH_3-N)
Mobile Emissions		
Baltimore City & Baltimore County	151	121
Maryland (entire state)	707	520
Total Emissions		
Baltimore City & Baltimore County	N/A	2,730
Maryland (entire state)	N/A	37,776

* Metric tons per year

Figures

Figure 5.1 Ammonia emissions by source for the state of Maryland.

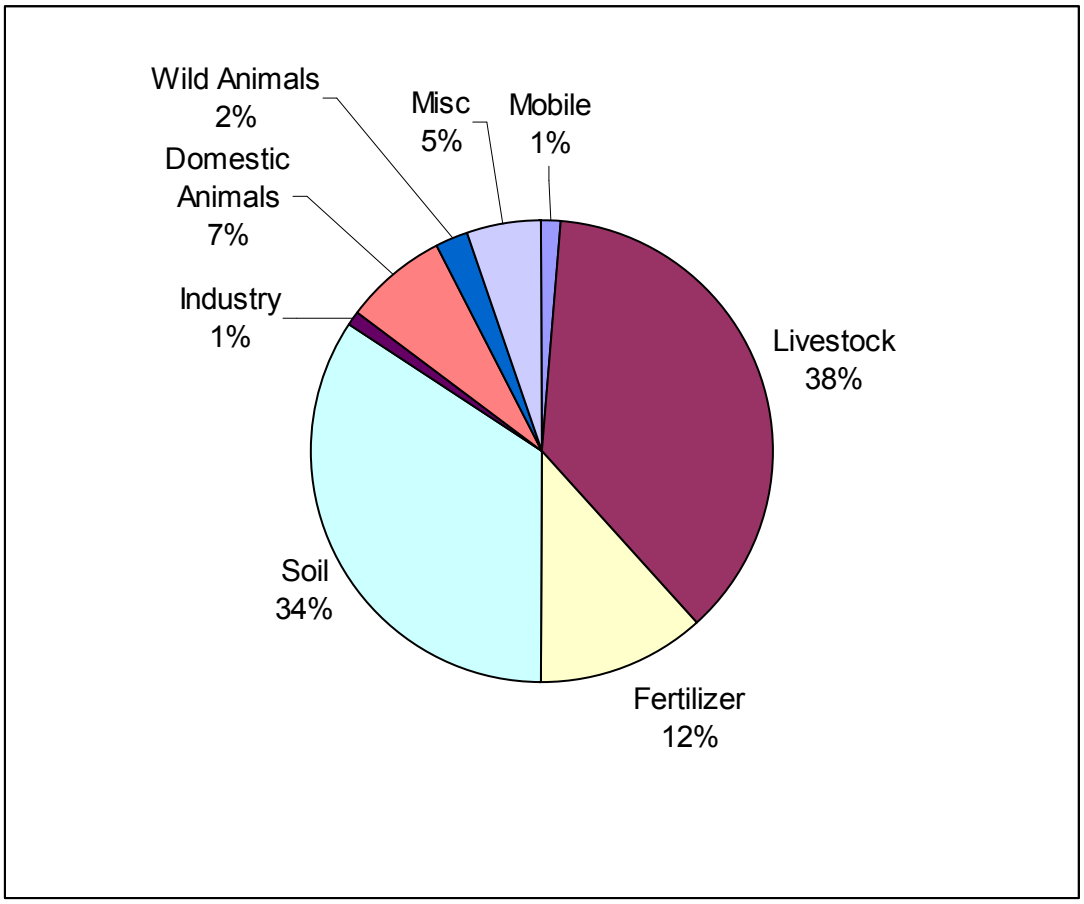


Figure 5.2 Ammonia emissions by source for Baltimore City and Baltimore County, Maryland.

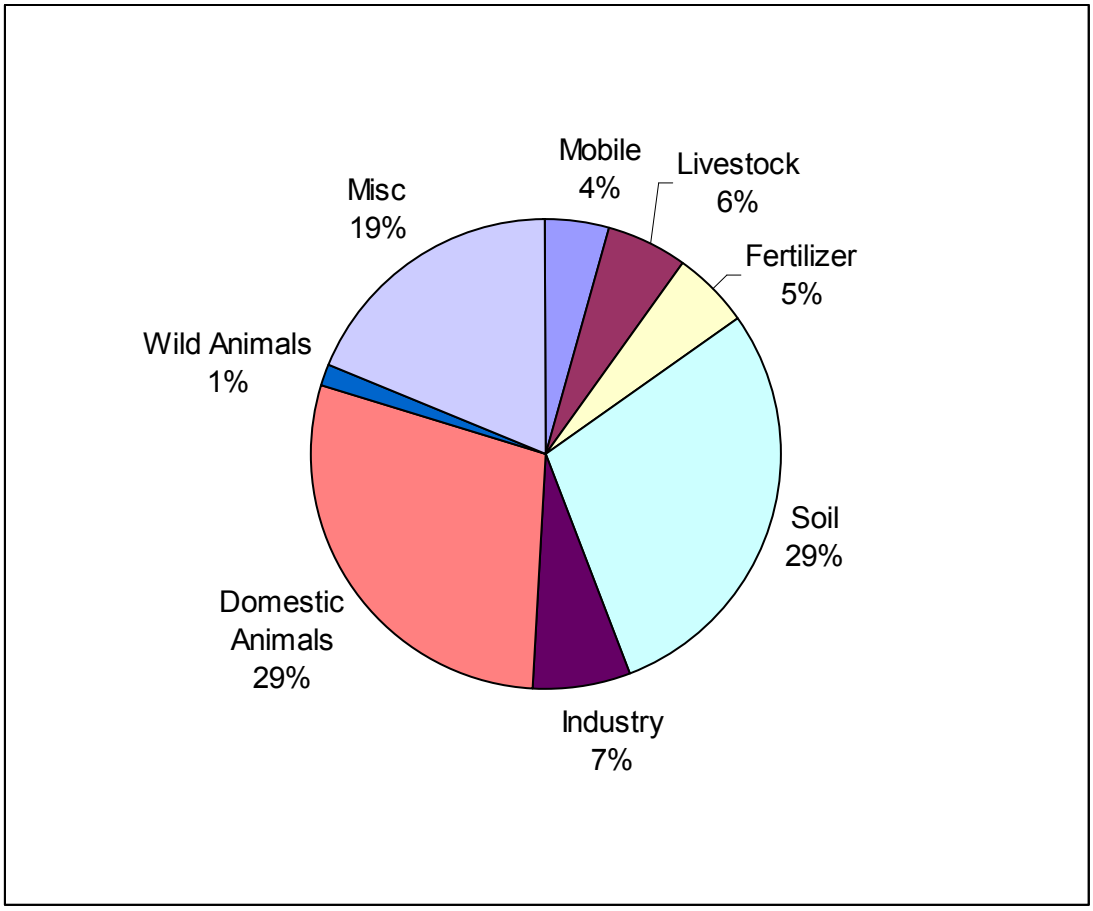


Figure 5.3 Total ammonia emissions by county for the state of Maryland.

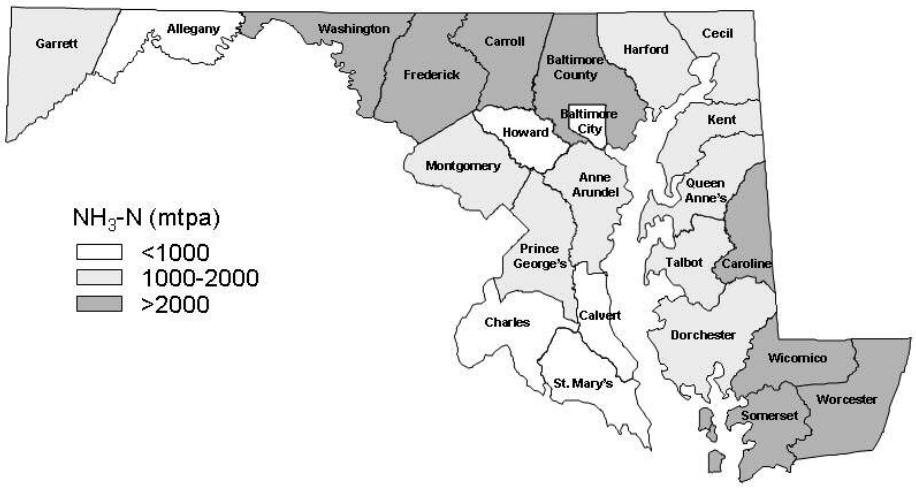
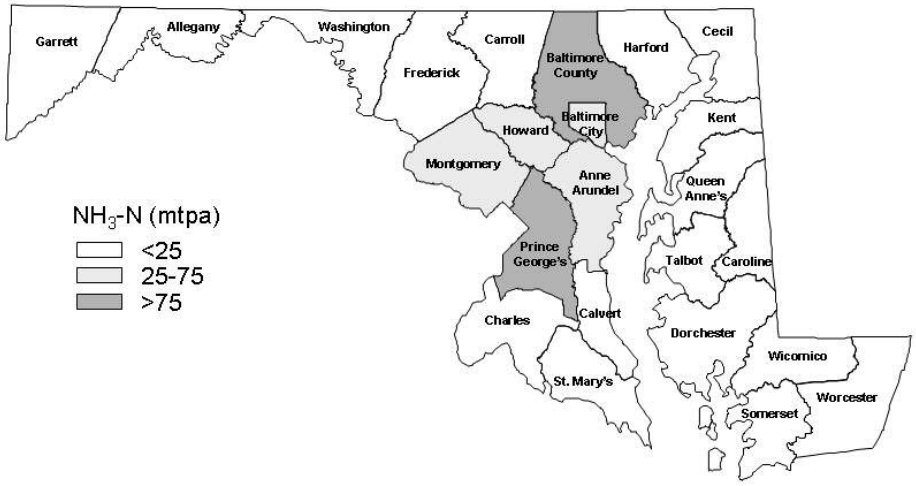


Figure 5.4 Mobile ammonia emissions by county for the state of Maryland.



Appendix A: Analysis of Error

Error was calculated by propagating known measurement error through the emission rate calculation. The method used is detailed in Principles of Instrumental Analysis (Skoog, 1985). Error is propagated using the following method:

If $A = B * C$,

Then $\Delta A^2 = (\delta A/\delta B)^2 * \Delta B^2 + (\delta A/\delta C)^2 * \Delta C^2$

Where ΔA, ΔB, ΔC *are the uncertainties associated with each variable, and* $\delta A/\delta B$ *and* $\delta A/\delta C$ *are the partial derivatives of* A *with respect to* B *and* C

Each step of this calculation is detailed in this appendix. Variables used are listed below.

Variable	**Name and Units**
A	Tunnel area (m^2)
C	Air ammonia concentration ($\mu g\ NH_3\text{-}N\ m^{-3}$)
D	Dilution volume (L)
E	Emission rate ($mg\ NH_3\text{-}N\ veh^{-1}\ km^{-1}$)
F	Airflow rate ($m^3\ s^{-1}$)
G	Gilibrator reading ($m^3\ s^{-1}$)
L	Tunnel length (km)
M	Mass flow rate ($\mu g\ NH_3\text{-}N\ s^{-1}$)
MN	Moles extracted (μmoles)

N	Ammonium concentration (μM)
Q	Ammonia generated (μg NH_3-N s^{-1})
T	Time deployed (minutes)
U	Air velocity (m s^{-1})
V	Air volume (m^3)

Flow Rate Error

Flow rate (F) in m^3 s^{-1} was calculated by multiplying the average air velocity (U) in m s^{-1} by the tunnel area (A) in m^2. The know error associated with the air velocity is given by EXTECH, the manufacturer of the anemometers, as ± 3% ± 0.1 m s^{-1}. Because of the uncertainty in tunnel air velocity due to the velocity profile model, a final error of 15% was applied to the air velocity (Appendix B). The error associated with the tunnel area was estimated to be 5%.

Flow rate error was calculated for each measurement location on each sampling date as:

$$\Delta F^2 = (\delta F/\delta U)^2 * \Delta U^2 + (\delta F/\delta A)^2 * \Delta A^2$$

$$= A^2 * \Delta U^2 + U^2 * \Delta A^2$$

Actual values are presented in Table A.1.

Air Volume Error

Air volume (V) in m^3 was calculated by multiplying the number of minutes deployed (T) by the average Gilibrator flow reading (G) in m^3 s^{-1}. The error associated with the

number of minutes deployed was estimated to be 1%. The error associated with the Gilibrator reading was 1%.

Air volume error was calculated for each measurement location on each sampling date as:

$$\Delta V^2 = (\delta V/\delta T)^2 * \Delta T^2 + (\delta V/\delta G)^2 * \Delta G^2$$

$$= G^2 * \Delta T^2 + T^2 * \Delta G^2$$

Actual values are presented in Table A.2.

Moles of Ammonia Extracted Error

The number of moles extracted (MN) in μmoles was calculated by multiplying the ammonium concentration (N) in μM by the dilution volume (D) in liters. The blank ammonium concentration was subtracted from each ammonium concentration calculated. The ammonium concentration was measured using one of three techniques (Chapter 4, Methods Section) and was assigned an estimated error of 10%. The error associated with the dilution volume was estimated to be ± 0.0005 L.

Moles extracted error was calculated for each measurement at each measurement location on each sampling date as:

$$\Delta MN^2 = (\delta MN/\delta N)^2 * \Delta N^2 + (\delta MN/\delta D)^2 * \Delta D^2$$

$$= D^2 * \Delta N^2 + N^2 * \Delta D^2$$

Actual values are presented in Tables A.3A, A.3B, A.3C, and A.3D. Error was calculated for each individual measurement which included two denuder extractions and two extractions for each filter at each location as well as a full extraction for the blank apparatus.

Air Ammonia Concentration Error

The ammonia concentration in the tunnel air (C) in μg NH_3-N m^{-3} was calculated by multiplying the total moles extracted (MN) in μmoles by the molecular weight of NH_3-N (14.01 μg $\mu mole^{-1}$) and then dividing by the total air volume (V) in m^3. The error associated with both the moles extracted and the total air volume was calculated in a previous step.

Ammonia concentration error was calculated at each measurement location for total, gas, and particulate forms of NH_3 on each sampling date as:

$$\Delta C^2 = (\delta C/\delta MN)^2 * \Delta MN^2 + (\delta C/\delta V)^2 * \Delta V^2$$

$$= (14.01/V)^2 * \Delta MN^2 + (-14.01 * MN/V^2)^2 * \Delta V^2$$

Actual values are presented in Table A.4.

Ammonia Mass Flow Rate Error

The mass flow rate (M) in μg NH_3-N s^{-1} was calculated by multiplying the total ammonia concentration in the air (C) in μg NH_3-N m^{-3} by the airflow rate (F) in m^3 s^{-1}. The error associated with both the ammonia concentration and the air flow rate was calculated in a previous step.

Mass flow rate error was calculated at each measurement location for total, gas, and particulate forms of NH_3 on each sampling date as:

$$\Delta M^2 = (\delta M/\delta C)^2 * \Delta C^2 + (\delta M/\delta F)^2 * \Delta F^2$$

$$= F^2 * \Delta C^2 + C^2 * \Delta F^2$$

Actual values are presented in Table A.5.

Ammonia Generated in Tunnel Error

The ammonia generated in the tunnel (Q) in mg NH_3-N s^{-1} was calculated by subtracting the sum of all incoming mass flow rates from the outgoing mass flow rate in μg NH_3-N s^{-1}. The error associated with mass flow rate was calculated in a previous step. There are four different mass flow rates used in this calculation, exit exhaust, entrance exhaust, entrance ventilation, and exit ventilation.

Ammonia generated in the tunnel error was calculated for total, gas, and particulate forms of NH_3 on each sampling date as:

$$\Delta Q^2 = (M_1^2 + M_2^2 + M_3^2 + M_4^2)/1000$$

Actual values are presented in Table A.6.

Ammonia Emission Rate Error

The emission rate (E) in mg NH_3-N veh^{-1} km^{-1} was calculated by dividing the total ammonia generated in the tunnel (Q) in mg NH_3-N s^{-1} by the vehicle rate (R) in veh s^{-1} and then by the tunnel length (L) in km. The error associated with the total

ammonia generated was calculated in a previous step. The error associated with the vehicle rate was estimated to be ± 0.005 veh s^{-1}. The error associated with the tunnel length was estimated to be ± 0.05 km.

The emission rate in the tunnel error was calculated for total, gas, and particulate forms of NH_3 on each sampling date as:

$$\Delta E^2 = (\delta E/\delta Q)^2 * \Delta Q^2 + (\delta E/\delta R)^2 * \Delta R^2 + (\delta E/\delta L)^2 * \Delta L^2$$

$$= (1/R/L)^2 * \Delta Q^2 + (-Q/R^2/L)^2 * \Delta R^2 + (-Q/R/L^2)^2 * \Delta L^2$$

Actual values are presented in Table A.7.

Tables

Table A.1 Average velocity, tunnel area, airflow rate, and their associated uncertainties (Δ) for all sampling locations in the Fort McHenry Tunnel, Baltimore, Maryland on four sampling dates. A - Air entering with vehicles, B - West ventilation air, D - East ventilation air, C - Air exiting with vehicles (Figure 4.1)

Sampling Date	Sampling Location	Average Air Velocity (U) ($m\ s^{-1}$)	ΔU	Tunnel Area (A) (m^2)	ΔA	Airflow Rate (F) ($m^3\ s^{-1}$)	ΔF
29 Sep 2003	A	4.74	0.24	54.74	2.74	260.30	18.60
	B	2.83	0.26	12.70	0.64	35.89	2.95
	C	5.36	0.18	54.74	2.74	299.10	20.79
	D	2.80	0.18	12.70	0.64	35.50	2.93
14 Nov 2003	A	5.48	0.27	54.74	2.74	301.32	20.92
	B	2.72	0.18	12.70	0.64	34.53	2.88
	C	6.73	0.31	54.74	2.74	375.71	25.17
	D	2.82	0.18	12.70	0.64	35.82	2.95
22 Mar 2004	A	5.22	0.26	54.74	2.74	286.61	20.08
	B	2.44	0.17	12.70	0.64	31.01	2.69
	C	6.03	0.28	54.74	2.74	336.64	22.93
	D	3.98	0.22	12.70	0.64	50.53	3.76
10 Jun 2004	A	5.78	0.27	54.74	2.74	317.56	21.84
	B	1.86	0.16	12.70	0.64	23.65	2.31
	C	6.50	0.30	54.74	2.74	362.80	24.43
	D	3.99	0.22	12.70	0.64	50.70	3.77

Table A.2 Gilibrator flow reading, minutes deployed, air volume, and their associated uncertainties (Δ) for all sampling locations in the Fort McHenry Tunnel, Baltimore, Maryland on four sampling dates.

Sampling Date	Sampling Location	Gilibrator Reading (G) ($m^3 s^{-1}$)	ΔG	Minutes Deployed (T) (min)	ΔT	Air Volume (V) (m^3)	ΔV
29 Sep 2003	Entrance Exhaust	10.10	0.10	375	3.75	3.79	0.05
	Exit Exhaust	10.00	0.10	287	2.87	2.87	0.04
	Fresh Air	10.15	0.10	282	2.82	2.86	0.04
14 Nov 2003	Entrance Exhaust	10.05	0.10	180	1.8	1.81	0.03
	Exit Exhaust	10.10	0.10	180	1.8	1.82	0.03
	Fresh Air	10.00	0.10	180	1.8	1.80	0.03
22 Mar 2004	Entrance Exhaust	10.10	0.10	180	1.8	1.82	0.03
	Exit Exhaust	10.15	0.10	180	1.8	1.83	0.03
	Fresh Air	10.10	0.10	180	1.8	1.82	0.03
10 Jun 2004	Entrance Exhaust	9.97	0.10	210	2.1	2.09	0.03
	Exit Exhaust	9.67	0.10	210	2.1	2.03	0.03
	Fresh Air	9.97	0.10	210	2.1	2.09	0.03

Table A.3A Ammonium concentration, dilution volume, moles extracted, and their associated uncertainties (Δ) for all sampling locations in the Fort McHenry Tunnel, Baltimore, Maryland on September 29, 2003.

Sampling Location	NH_3 Form	Part of Apparatus Extracted*	Ammonium Concentration (N) (μM)	ΔN	Dilution Volume (D) (L)	ΔD	Moles Extracted (MN) (μmoles)	ΔMN
Entrance Exhaust	Total						3.36	0.30
	Gas	Denuder I	143.25	14.32	0.02	0.0005	2.86	0.30
		Denuder II	0.00	0.00	0.00	0.0000	0.00	0.00
						Gas Total	2.86	0.30
						Gas Total - Blank	2.80	0.30
	Particulate	Zefluor I	14.33	1.43	0.02	0.0005	0.29	0.03
		Zefluor II	0.00	0.00	0.00	0.0000	0.00	0.00
		Nylasorb I	0.00	0.00	0.00	0.0000	0.00	0.00
		Nylasorb II	0.00	0.00	0.00	0.0000	0.00	0.00
		Quartz I	18.27	1.83	0.02	0.0005	0.37	0.04
		Quartz II	0.00	0.00	0.00	0.0000	0.00	0.00
						Particulate Total	0.65	0.05
						Particulate Total - Blank	0.56	0.05
Exit Exhaust	Total						9.67	0.96
	Gas	Denuder I	463.92	46.39	0.02	0.0005	9.28	0.96
		Denuder II	0.00	0.00	0.00	0.0000	0.00	0.00
						Gas Total	9.28	0.96
						Gas Total - Blank	9.22	0.96

Table A.3A Continued

Sampling Location	NH_3 Form	Part of Apparatus Extracted*	Ammonium Concentration (N) (μM)	ΔN	Dilution Volume (D) (L)	ΔD	Moles Extracted (MN) (μmoles)	ΔMN
	Particulate	Zefluor I	11.70	1.17	0.02	0.0005	0.23	0.02
		Zefluor II	0.00	0.00	0.00	0.0000	0.00	0.00
		Nylasorb I	0.00	0.00	0.00	0.0000	0.00	0.00
		Nylasorb II	0.00	0.00	0.00	0.0000	0.00	0.00
		Quartz I	15.41	1.54	0.02	0.0005	0.31	0.03
		Quartz II	0.00	0.00	0.00	0.0000	0.00	0.00
						Particulate Total	0.54	0.04
						Particulate Total - Blank	0.45	0.04
Fresh Air	Total						1.25	0.11
	Gas	Denuder I	51.41	5.14	0.02	0.0005	1.03	0.11
		Denuder II	0.00	0.00	0.00	0.0000	0.00	0.00
						Gas Total	1.03	0.11
						Gas Total - Blank	0.97	0.11
	Particulate	Zefluor I	9.71	0.97	0.02	0.0005	0.19	0.02
		Zefluor II	0.00	0.00	0.00	0.0000	0.00	0.00
		Nylasorb I	0.00	0.00	0.00	0.0000	0.00	0.00
		Nylasorb II	0.00	0.00	0.00	0.0000	0.00	0.00
		Quartz I	8.95	0.89	0.02	0.0005	0.18	0.02
		Quartz II	0.00	0.00	0.00	0.0000	0.00	0.00
						Particulate Total	0.37	0.03
						Particulate Total - Blank	0.28	0.03

Table A.3A Continued

Sampling Location	NH_3 Form	Part of Apparatus Extracted*	Ammonium Concentration (N) (μM)	ΔN	Dilution Volume (D) (L)	ΔD	Moles Extracted (MN) (μmoles)	ΔMN
Blank	Total						0.16	0.01
	Gas	Denuder I	3.14	0.31	0.02	0.0005	0.06	0.01
		Denuder II	0.00	0.00	0.00	0.0000	0.00	0.00
						Blank Total	0.06	0.01
	Particulate	Zefluor I	0.00	0.00	0.02	0.0005	0.00	0.00
		Zefluor II	0.00	0.00	0.00	0.0000	0.00	0.00
		Nylasorb I	0.00	0.00	0.00	0.0000	0.00	0.00
		Nylasorb II	0.00	0.00	0.00	0.0000	0.00	0.00
		Quartz I	4.62	0.46	0.02	0.0005	0.09	0.01
		Quartz II	0.00	0.00	0.00	0.0000	0.00	0.00
						Blank Total	0.09	0.01

* Roman numerals following apparatus part indicate which extraction is included in the measurement.

Table A.3B Ammonium concentration, dilution volume, moles extracted, and their associated uncertainties (Δ) for all sampling locations in the Fort McHenry Tunnel, Baltimore, Maryland on November 14, 2003.

Sampling Location	NH_3 Form	Part of Apparatus Extracted*	Ammonium Concentration (N) (μM)	ΔN	Dilution Volume (D) (L)	ΔD	Moles Extracted (MN) (μmoles)	ΔMN
Entrance Exhaust	Total						0.84	0.07
	Gas	Denuder I	35.10	3.51	0.02	0.0005	0.80	0.07
		Denuder II	5.20	0.52	0.01	0.0005	0.03	0.01
						Gas Total	0.75	0.07
						Gas Total - Blank	0.71	0.07
	Particulate	Zefluor I						
		Zefluor II	0.00	0.00	0.02	0.0005	0.04	0.00
		Nylasorb I	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb II	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz I	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz II	6.48	0.65	0.02	0.0005	0.20	0.01
			0.00	0.00	0.02	0.0005	0.00	0.00
						Particulate Total	0.13	0.01
						Particulate Total - Blank	0.13	0.01
Exit Exhaust	Total						5.10	0.34
			89.77	8.98	0.02	0.0005	1.80	0.19
	Gas	Denuder I	8.68	0.87	0.01	0.0005	0.09	0.01
		Denuder II				Gas Total	1.88	0.19
						Gas Total - Blank	1.84	0.19

Table A.3B Continued

Sampling Location	NH_3 Form	Part of Apparatus Extracted*	Ammonium Concentration (N) (μM)	ΔN	Dilution Volume (D) (L)	ΔD	Moles Extracted (MN) (μmoles)	ΔMN
	Particulate	Zefluor I	1.58	0.16	0.02	0.0005	0.03	0.00
		Zefluor II	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb I	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb II	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz I	135.97	13.60	0.02	0.0005	2.72	0.28
		Quartz II	25.47	2.55	0.02	0.0005	0.51	0.05
						Particulate Total	3.26	0.29
						Particulate Total - Blank	3.26	0.29
Fresh Air	Total						1.02	0.09
	Gas	Denuder I	39.98	4.00	0.02	0.0005	0.00	0.08
		Denuder II	2.69	0.27	0.01	0.0005	0.00	0.00
						Gas Total	0.83	0.08
						Gas Total - Blank	0.78	0.08
	Particulate	Zefluor I	2.09	0.21	0.02	0.0005	0.00	0.00
		Zefluor II	0.00	0.00	0.02	0.0005	0.13	0.00
		Nylasorb I	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb II	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz I	9.93	0.99	0.02	0.0005	0.20	0.02
		Quartz II	0.00	0.00	0.02	0.0005	0.00	0.00
						Particulate Total	0.24	0.02
						Particulate Total - Blank	0.24	0.02

Table A.3B Continued

Sampling Location	NH_3 Form	Part of Apparatus Extracted*	Ammonium Concentration (N) (μM)	ΔN	Dilution Volume (D) (L)	ΔD	Moles Extracted (MN) (μmoles)	ΔMN
Blank	Total						0.05	0.00
	Gas	Denuder I	2.33	0.23	0.02	0.0005	0.05	0.00
		Denuder II	0.00	0.00	0.01	0.0005	0.00	0.00
						Blank Total	0.05	0.00
	Particulate	Zefluor I	0.00	0.00	0.02	0.0005	0.00	0.00
		Zefluor II	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb I	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb II	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz I	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz II	0.00	0.00	0.02	0.0005	0.00	0.00
						Blank Total	0.00	0.00

* Roman numerals following apparatus part indicate which extraction is included in the measurement.

Table A.3C Ammonium concentration, dilution volume, moles extracted, and their associated uncertainties (Δ) for all sampling locations in the Fort McHenry Tunnel, Baltimore, Maryland on March 22, 2004.

Sampling Location	NH_3 Form	Part of Apparatus Extracted*	Ammonium Concentration (N) (μM)	ΔN	Dilution Volume (D) (L)	ΔD	Moles Extracted (MN) (μmoles)	ΔMN
Entrance Exhaust	Total						0.61	0.06
	Gas	Denuder I	15.25	1.53	0.04	0.0005	0.61	0.06
		Denuder II	0.00	0.00	0.01	0.0005	0.00	0.00
						Gas Total	0.61	0.06
						Gas Total - Blank	0.61	0.06
	Particulate	Zefluor I	0.00	0.00	0.02	0.0005	0.00	0.00
		Zefluor II	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb I	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb II	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz I	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz II	0.00	0.00	0.02	0.0005	0.00	0.00
						Particulate Total	0.00	0.00
						Particulate Total - Blank	0.00	0.00
Exit Exhaust	Total						1.46	0.14
		Denuder I	17.69	1.77	0.08	0.0005	1.42	0.14
	Gas	Denuder II	0.63	0.06	0.01	0.0005	0.01	0.00
						Gas Total	1.42	0.14
						Gas Total - Blank	1.42	0.14

Table A.3C Continued

Sampling Location	NH_3 Form	Part of Apparatus Extracted*	Ammonium Concentration (N) (μM)	ΔN	Dilution Volume (D) (L)	ΔD	Moles Extracted (MN) (μmoles)	ΔMN
	Particulate	Zefluor I	0.00	0.00	0.02	0.0005	0.00	0.00
		Zefluor II	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb I	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb II	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz I	1.98	0.20	0.02	0.0005	0.04	0.00
		Quartz II	0.00	0.00	0.02	0.0005	0.00	0.00
						Particulate Total	0.04	0.00
						Particulate Total - Blank	0.04	0.00
Fresh Air	Total							
							0.03	0.00
	Gas	Denuder I	1.46	0.15	0.02	0.0005	0.03	0.00
		Denuder II	0.00	0.00	0.01	0.0005	0.00	0.00
						Gas Total	0.03	0.00
						Gas Total - Blank	0.03	0.00
	Particulate	Zefluor I	0.00	0.00	0.02	0.0005	0.00	0.00
		Zefluor II	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb I	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb II	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz I	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz II	0.00	0.00	0.02	0.0005	0.00	0.00
						Particulate Total	0.00	0.00
						Particulate Total - Blank	0.00	0.00

Table A.3C Continued

Sampling Location	NH_3 Form	Part of Apparatus Extracted*	Ammonium Concentration (N) (μM)	ΔN	Dilution Volume (D) (L)	ΔD	Moles Extracted (MN) (μmoles)	ΔMN
Blank	Total						0.00	0.00
	Gas	Denuder I	0.00	0.00	0.02	0.0005	0.00	0.00
		Denuder II	0.00	0.00	0.01	0.0005	0.00	0.00
						Blank Total	0.00	0.00
	Particulate	Zefluor I	0.00	0.00	0.02	0.0005	0.00	0.00
		Zefluor II	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb I	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb II	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz I	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz II	0.00	0.00	0.02	0.0005	0.00	0.00
						Blank Total	0.00	0.00

* Roman numerals following apparatus part indicate which extraction is included in the measurement.

Table A.3D Ammonium concentration, dilution volume, moles extracted, and their associated uncertainties (Δ) for all sampling locations in the Fort McHenry Tunnel, Baltimore, Maryland on June 10, 2004.

Sampling Location	NH_3 Form	Part of Apparatus Extracted*	Ammonium Concentration (N) (μM)	ΔN	Dilution Volume (D) (L)	ΔD	Moles Extracted (MN) (μmoles)	ΔMN
Entrance Exhaust	Total						1.89	0.16
	Gas	Denuder I	76.84	7.68	0.02	0.0005	1.54	0.16
		Denuder II	10.85	1.09	0.01	0.0005	0.11	0.01
						Gas Total	1.65	0.16
						Gas Total - Blank	1.59	0.16
	Particulate	Zefluor I	11.55	1.16	0.02	0.0005	0.23	0.02
		Zefluor II	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb I	2.60	0.26	0.02	0.0005	0.05	0.01
		Nylasorb II	1.67	0.17	0.02	0.0005	0.03	0.00
		Quartz I	0.81	0.08	0.02	0.0005	0.02	0.00
		Quartz II	0.24	0.02	0.02	0.0005	0.00	0.00
						Particulate Total	0.34	0.02
						Particulate Total - Blank	0.30	0.02
Exit Exhaust	Total						4.75	0.42
	Gas	Denuder I	203.00	20.30	0.02	0.0005	4.06	0.42
		Denuder II	26.10	2.61	0.01	0.0005	0.26	0.03
						Gas Total	4.32	0.42
						Gas Total - Blank	4.27	0.42

Table A.3D Continued

Sampling Location	NH_3 Form	Part of Apparatus Extracted*	Ammonium Concentration (N) (μM)	ΔN	Dilution Volume (D) (L)	ΔD	Moles Extracted (MN) (μmoles)	ΔMN
	Particulate	Zefluor I	13.96	1.40	0.02	0.0005	0.28	0.03
		Zefluor II	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb I	4.73	0.47	0.02	0.0005	0.09	0.01
		Nylasorb II	1.43	0.14	0.02	0.0005	0.03	0.00
		Quartz I	5.58	0.56	0.02	0.0005	0.11	0.01
		Quartz II	0.11	0.01	0.02	0.0005	0.00	0.00
						Particulate Total	0.52	0.03
						Particulate Total - Blank	0.48	0.03
Fresh Air	Total						1.26	0.10
	Gas	Denuder I	46.35	4.64	0.02	0.0005	0.93	0.10
		Denuder II	4.42	0.44	0.01	0.0005	0.04	0.00
						Gas Total	0.97	0.10
						Gas Total - Blank	0.92	0.10
	Particulate	Zefluor I	11.26	1.13	0.02	0.0005	0.23	0.02
		Zefluor II	0.00	0.00	0.02	0.0005	0.00	0.00
		Nylasorb I	2.62	0.26	0.02	0.0005	0.05	0.01
		Nylasorb II	2.00	0.20	0.02	0.0005	0.04	0.00
		Quartz I	2.84	0.28	0.02	0.0005	0.06	0.01
		Quartz II	0.54	0.05	0.02	0.0005	0.01	0.00
						Particulate Total	0.32	0.02
						Particulate Total - Blank	0.35	0.03

Table A.3D Continued

Sampling Location	NH_3 Form	Part of Apparatus Extracted*	Ammonium Concentration (N) (μM)	ΔN	Dilution Volume (D) (L)	ΔD	Moles Extracted (MN) (μmoles)	ΔMN
Blank	Total						0.09	0.01
Gas	Gas	Denuder I	2.16	0.22	0.02	0.0005	0.04	0.00
		Denuder II	0.96	0.10	0.01	0.0005	0.01	0.00
						Blank Total	0.05	0.00
Particulate	Particulate	Zefluor I	0.34	0.03	0.02	0.0005	0.01	0.00
		Zefluor II	0.00	0.00	0.02	0.0005	0.00	0.00
		Quartz I	1.61	0.16	0.02	0.0005	0.03	0.00
						Blank Total	0.04	0.00

* Roman numerals following apparatus part indicate which extraction is included in the measurement.

Table A.4 Moles extracted, total air volume, tunnel air ammonia concentration, and their associated uncertainties (Δ) for both gas and particulate forms of NH_3 and total at all sampling locations in the Fort McHenry Tunnel, Baltimore, Maryland on four sampling dates.

Sampling Date	Sampling Location	NH_3 Form	Moles Extracted (MN) (μmoles)	ΔMN	Total Air Volume (V) (m^3)	ΔV	Air Ammonia Concentration (C) (μg NH_3-N m^{-3})	ΔC
29 Sep 2003	Entrance Exhaust	Total	3.36	0.30	3.79	0.05	12.44	1.12
		Gas	2.80	0.30	3.79	0.05	10.37	1.10
		Particulate	0.56	0.05	3.79	0.05	2.07	0.18
	Exit Exhaust	Total	9.67	0.96	2.87	0.04	47.18	4.72
		Gas	9.22	0.96	2.87	0.04	44.99	4.71
		Particulate	0.45	0.04	2.87	0.04	2.20	0.20
	Fresh Air	Total	1.25	0.11	2.86	0.04	6.10	0.54
		Gas	0.97	0.11	2.86	0.04	4.73	0.52
		Particulate	0.28	0.03	2.86	0.04	1.37	0.14
14 Nov 2003	Entrance Exhaust	Total	0.84	0.07	1.81	0.03	6.48	0.58
		Gas	0.71	0.07	1.81	0.03	5.48	0.57
		Particulate	0.13	0.01	1.81	0.03	1.00	0.10
	Exit Exhaust	Total	5.10	0.34	1.82	0.03	39.27	2.65
		Gas	1.84	0.19	1.82	0.03	14.14	1.44
		Particulate	3.26	0.29	1.82	0.03	25.13	2.23
	Fresh Air	Total	1.02	0.09	1.80	0.03	7.94	0.67

Table A.4 Continued

Sampling Date	Sampling Location	NH_3 Form	Moles Extracted (MN) (μmoles)	ΔMN	Total Air Volume (V) (m^3)	ΔV	Air Ammonia Concentration (C) (μg NH_3-N m^{-3})	ΔC
		Gas	0.78	0.08	1.80	0.03	6.07	0.65
		Particulate	0.24	0.02	1.80	0.03	1.87	0.16
22 Mar 2004	Entrance Exhaust	Total	0.61	0.06	1.82	0.03	4.70	0.48
		Gas	0.61	0.06	1.82	0.03	4.70	0.48
		Particulate	0.00	0.00	1.82	0.03	0.00	0.00
	Exit Exhaust	Total	1.46	0.14	1.83	0.03	11.20	1.10
		Gas	1.42	0.14	1.83	0.03	10.90	1.10
		Particulate	0.04	0.00	1.83	0.03	0.30	0.03
	Fresh Air	Total	0.03	0.00	1.82	0.03	0.23	0.02
		Gas	0.03	0.00	1.82	0.03	0.23	0.02
		Particulate	0.00	0.00	1.82	0.03	0.00	0.00
10 Jun 2004	Entrance Exhaust	Total	1.89	0.16	2.09	0.03	12.65	1.09
		Gas	1.59	0.16	2.09	0.03	10.66	1.07
		Particulate	0.30	0.02	2.09	0.03	2.00	0.17
	Exit Exhaust	Total	4.75	0.42	2.03	0.03	32.74	2.93
		Gas	4.27	0.42	2.03	0.03	29.45	2.92
		Particulate	0.48	0.03	2.03	0.03	3.29	0.23

Table A.4 Continued

Sampling Date	Sampling Location	NH_3 Form	Moles Extracted (MN) (μmoles)	ΔMN	Total Air Volume (V) (m^3)	ΔV	Air Ammonia Concentration (C) (μg NH_3-N m^{-3})	ΔC
	Fresh Air	Total	1.26	0.10	2.09	0.03	8.46	0.67
		Gas	0.92	0.10	2.09	0.03	6.14	0.65
		Particulate	0.35	0.03	2.09	0.03	2.32	0.17

Table A.5 Tunnel air ammonia concentration, air flow rate, mass flow rate, and their associated uncertainties (Δ) for both gas and particulate forms of NH_3 and total at all sampling locations in the Fort McHenry Tunnel, Baltimore, Maryland on four sampling dates.

Sampling Date	Sampling Location	NH_3 Form	Air Ammonia Concentration (C) ($\mu g\ NH_3\text{-}N\ m^{-3}$)	ΔC	Air Flow Rate (F) ($m^3\ s^{-1}$)	ΔF	Mass Flow Rate (M) ($\mu g\ NH_3\text{-}N\ s^{-1}$)	ΔM
29 Sep 2003	Entrance Exhaust	Total	12.44	1.12	259.28	41.00	3224.14	586.36
		Gas	10.37	1.10	259.28	41.00	2687.41	512.10
		Particulate	2.07	0.18	259.28	41.00	536.73	97.21
	Exit Exhaust	Total	47.18	4.72	54.74	46.36	13834.47	2202.60
		Gas	44.99	4.71	54.74	46.36	13190.59	2101.50
		Particulate	2.20	0.20	54.74	46.36	643.88	102.41
	Entrance Ventilation	Total	6.10	0.54	12.70	5.67	218.92	35.30
		Gas	4.73	0.52	12.70	5.67	169.60	27.63
		Particulate	1.37	0.14	12.70	5.67	49.32	8.01
	Exit Ventilation	Total	6.10	0.54	12.70	5.61	216.53	34.92
		Gas	4.73	0.52	12.70	5.61	167.75	27.35
		Particulate	1.37	0.14	12.70	5.61	48.78	7.92
14 Nov 2003	Entrance Exhaust	Total	6.48	0.58	300.14	47.46	1945.48	353.19
		Gas	5.48	0.57	300.14	47.46	1644.14	311.00
		Particulate	1.00	0.10	300.14	47.46	301.34	57.04

Table A.5 Continued

Sampling Date	Sampling Location	NH_3 Form	Air Ammonia Concentration (C) ($\mu g\ NH_3\text{-}N\ m^{-3}$)	ΔC	Air Flow Rate (F) ($m^3\ s^{-1}$)	ΔF	Mass Flow Rate (M) ($\mu g\ NH_3\text{-}N\ s^{-1}$)	ΔM
	Exit Exhaust	Total	39.27	2.65	368.31	58.24	14464.29	2486.99
		Gas	14.14	1.44	368.31	58.24	5209.71	980.21
		Particulate	25.13	2.23	368.31	58.24	9254.58	1677.39
	Entrance Ventilation	Total	7.94	0.67	34.53	5.46	274.22	49.14
		Gas	6.07	0.65	34.53	5.46	209.61	40.00
		Particulate	1.87	0.16	34.53	5.46	64.61	11.70
	Exit Ventilation	Total	7.94	0.67	35.82	5.66	284.46	50.97
		Gas	6.07	0.65	35.82	5.66	217.43	41.50
		Particulate	1.87	0.16	35.82	5.66	67.03	12.13
22 Mar 2004	Entrance Exhaust	Total	4.70	0.48	285.49	45.14	1342.11	252.36
		Gas	4.70	0.48	285.49	45.14	1342.11	252.36
		Particulate	0.00	0.00	285.49	45.14	0.00	0.00
	Exit Exhaust	Total	11.20	1.10	330.01	52.18	3697.55	687.94
		Gas	10.90	1.10	330.01	52.18	3597.48	674.47
		Particulate	0.30	0.03	330.01	52.18	100.07	18.94
	Entrance Ventilation	Total	0.23	0.02	31.01	4.90	7.00	1.32
		Gas	0.23	0.02	31.01	4.90	7.00	1.32
		Particulate	0.00	0.00	31.01	4.90	0.00	0.00

Table A.5 Continued

Sampling Date	Sampling Location	NH_3 Form	Air Ammonia Concentration (C) ($\mu g\ NH_3\text{-}N\ m^{-3}$)	ΔC	Air Flow Rate (F) ($m^3\ s^{-1}$)	ΔF	Mass Flow Rate (M) ($\mu g\ NH_3\text{-}N\ s^{-1}$)	ΔM
	Exit Ventilation	Total	0.23	0.02	50.53	7.99	11.41	2.16
		Gas	0.23	0.02	50.53	7.99	11.41	2.16
		Particulate	0.00	0.00	50.53	7.99	0.00	0.00
10 Jun 2004	Entrance Exhaust	Total	12.65	1.09	316.31	50.01	4002.49	720.29
		Gas	10.66	1.07	316.31	50.01	3370.53	632.03
		Particulate	2.00	0.17	316.31	50.01	631.96	113.36
	Exit Exhaust	Total	32.74	2.93	355.66	56.23	11643.89	2116.10
		Gas	29.45	2.92	355.66	56.23	10472.56	1955.38
		Particulate	3.29	0.23	355.66	56.23	1171.33	202.62
	Entrance Ventilation	Total	8.46	0.67	23.65	3.74	200.18	35.39
		Gas	6.14	0.65	23.65	3.74	145.34	27.61
		Particulate	2.32	0.17	23.65	3.74	2.32	9.57
	Exit Ventilation	Total	8.46	0.67	50.70	8.02	429.04	75.85
		Gas	6.14	0.65	50.70	8.02	311.51	59.17
		Particulate	2.32	0.17	50.70	8.02	117.53	20.52

Table A.6 Mass flow rate, total ammonia generated in the tunnel, and their associated uncertainties (Δ) for both gas and particulate forms of NH_3 and total at all sampling locations in the Fort McHenry Tunnel, Baltimore, Maryland on four sampling dates.

Sampling Date	Sampling Location	NH_3 Form	Mass Flow Rate (M) ($\mu g\ NH_3\text{-}N\ s^{-1}$)	ΔM	Ammonia Generated in Tunnel (Q) ($mg\ NH_3\text{-}N\ s^{-1}$)	ΔQ
29 Sep 2003	Entrance Exhaust	Total	3224.14	586.36		
		Gas	2687.41	512.10		
		Particulate	536.73	97.21		
	Exit Exhaust	Total	13834.47	2202.60		
		Gas	13190.59	2101.50		
		Particulate	643.88	102.41		
	Entrance Ventilation	Total	218.92	35.30		
		Gas	169.60	27.63		
		Particulate	49.32	8.01		
	Exit Ventilation	Total	216.53	34.92		
		Gas	167.75	27.35		
		Particulate	48.78	7.92		

	Total	
Total	10.17	2.28
Gas	10.17	2.16
Particulate	0.01	0.14

Table A.6 Continued

Sampling Date	Sampling Location	NH_3 Form	Mass Flow Rate (M) ($\mu g\ NH_3\text{-}N\ s^{-1}$)	ΔM	Ammonia Generated in Tunnel (Q) ($mg\ NH_3\text{-}N\ s^{-1}$)	ΔQ
14 Nov 2003	Entrance Exhaust	Total	1945.48	353.19		
		Gas	1644.14	311.00		
		Particulate	301.34	57.04		
	Exit Exhaust	Total	14464.29	2486.99		
		Gas	5209.71	980.21		
		Particulate	9254.58	1677.39		
	Entrance Ventilation	Total	274.22	49.14		
		Gas	209.61	40.00		
		Particulate	64.61	11.70		
	Exit Ventilation	Total	284.46	50.97		
		Gas	217.43	41.50		
		Particulate	67.03	12.13		
				Total		
				Total	11.96	2.51
				Gas	3.14	1.03
				Particulate	8.82	1.68
22 Mar 2004	Entrance Exhaust	Total	1342.11	252.36		
		Gas	1342.11	252.36		
		Particulate	0.00	0.00		

Table A.6 Continued

Sampling Date	Sampling Location	NH_3 Form	Mass Flow Rate (M) ($\mu g\ NH_3\text{-}N\ s^{-1}$)	ΔM	Ammonia Generated in Tunnel (Q) ($mg\ NH_3\text{-}N\ s^{-1}$)	ΔQ
	Exit Exhaust	Total	3697.55	687.94		
		Gas	3597.48	674.47		
		Particulate	100.07	18.94		
	Entrance Ventilation	Total	7.00	1.32		
		Gas	7.00	1.32		
		Particulate	0.00	0.00		
	Exit Ventilation	Total	11.41	2.16		
		Gas	11.41	2.16		
		Particulate	0.00	0.00		
					Total	
				Total	2.34	0.73
				Gas	2.24	0.72
				Particulate	0.10	0.02
10 Jun 2004	Entrance Exhaust	Total	4002.49	720.29		
		Gas	3370.53	632.03		
		Particulate	631.96	113.36		
	Exit Exhaust	Total	11643.89	2116.10		
		Gas	10472.56	1955.38		
		Particulate	1171.33	202.62		

Table A.6 Continued

Sampling Date	Sampling Location	NH_3 Form	Mass Flow Rate (M) ($\mu g\ NH_3\text{-}N\ s^{-1}$)	ΔM	Ammonia Generated in Tunnel (Q) ($mg\ NH_3\text{-}N\ s^{-1}$)	ΔQ
	Entrance Ventilation	Total	200.18	35.39		
		Gas	145.34	27.61		
		Particulate	2.32	9.57		
	Exit Ventilation	Total	429.04	75.85		
		Gas	311.51	59.17		
		Particulate	117.53	20.52		
					Total	
				Total	7.01	2.24
				Gas	6.65	2.06
				Particulate	0.37	0.23

Table A.7 Total ammonia generated in the tunnel, vehicle rate, tunnel length, and their associated uncertainties (Δ) for both gas and particulate forms of NH_3 and total at all sampling locations in the Fort McHenry Tunnel, Baltimore, Maryland on four sampling dates.

Sampling Date	NH_3 Form	Ammonia Generated in Tunnel (Q) (mg NH_3-N s^{-1})	ΔQ	Vehicle Rate (R) (veh s^{-1})	ΔR	Tunnel Length (L) (km)	ΔL	Emission Rate (E) (mg NH_3-N veh^{-1} km^{-1})	ΔE	Error %
29 Sep 2003	Total	10.17	2.28	0.52	0.01	1.90	0.05	10.2	2.3	23%
	Total (corrected)	10.17	2.28	0.51	0.01	1.90	0.05	10.5	2.4	23%
	Gas	10.17	2.16	0.52	0.01	1.90	0.05	10.2	2.2	21%
	Particulate	0.01	0.14	0.52	0.01	1.90	0.05	0.0	0.1	1566%
14 Nov 2003	Total	11.96	2.51	0.55	0.01	1.90	0.05	11.4	2.4	21%
	Total (corrected)	11.96	2.51	0.52	0.01	1.90	0.05	12.1	2.6	21%
	Gas	3.14	1.03	0.55	0.01	1.90	0.05	3.0	1.0	33%
	Particulate	8.82	1.68	0.55	0.01	1.90	0.05	8.4	1.6	19%
22 Mar 2004	Total	2.34	0.73	0.43	0.01	1.90	0.05	2.8	0.9	31%
	Total (corrected)	2.34	0.73	0.42	0.01	1.90	0.05	2.9	0.9	31%
	Gas	2.24	0.72	0.43	0.01	1.90	0.05	2.7	0.9	32%
	Particulate	0.10	0.02	0.43	0.01	1.90	0.05	0.1	0.0	19%
10 Jun 2004	Total	7.01	2.24	0.47	0.01	1.90	0.05	7.9	2.5	32%
	Total (corrected)	7.01	2.24	0.35	0.01	1.90	0.05	10.7	3.4	32%
	Gas	6.65	2.06	0.47	0.01	1.90	0.05	7.5	2.3	31%
	Particulate	0.37	0.23	0.47	0.01	1.90	0.05	0.4	0.3	64%

Appendix B: Velocity Profile

Velocity Profile Model

Velocity measurements were made in the tunnel using anemometers suspended 0.25 m from the ceiling. In order to determine the actual mean tunnel air velocity the tunnel was modeled as turbulent flow. The model used was taken from Perry's Chemical Engineers' Handbook (Green and Maloney, 1997). Parameters input into the model were as follows:

Tunnel diameter	= 10.52 m
Viscosity of air at 20 °C	= 3.26×10^{-5} kg m^{-1} s^{-1}
Density of air at 20 °C	= 1.2 kg m^{-3}
Reynolds Number	= 2.4×10^{6}
	= mean velocity * density * diameter / viscosity
Friction factor	= 3×10^{-3} (Table 6-9 from Perry's)
Wall stress	= 0.069 kg m^{-1} s^{-2}
	= friction factor * density * mean velocity^2 / 2
Friction velocity	= 0.240 m s^{-1}
	= (wall stress / density)$^{0.5}$

The graph of tunnel velocity vs. distance from wall representing the velocity profile for a mean tunnel velocity of 6.2 m s^{-1} is presented in figure B.1.

By changing the mean velocity in the model, the velocities at different distances from the tunnel walls also changed. Using an iterative process, the mean velocity was

changed until the velocity at .25 m was equal to the velocity measured on the anemometer. The mean velocity was then used to calculate an average correction factor over all the tunnel deployments (Table B.1). This correction factor was calculated for the velocity measured at the tunnel entrance and the velocity measured at the tunnel exit. The correction factor was then applied to the velocities measured in each deployment to approximate the actual tunnel mean velocity. The velocity was used to calculate the flow rate of air through the tunnel as a part of the emission rate calculation.

Measurement Error

To determine the error associated with this measurement, velocity was measured from the tunnel ceiling at the exit, and in the tunnel at the exit at car height approximately 0.8 m in from the tunnel walls during the pilot study conducted on July 29, 2003. Using the iterative method described previously, the ceiling velocity measurement of 5.94 m s^{-1} gave a mean tunnel velocity of 6.2 m s^{-1}. Using the model, the velocity measured 0.8 m from the wall was calculated to be 6.7 m s^{-1}. The actual value measured was 7.27 m s^{-1}. The difference between these two values was ~9%. Due to the error inherent in the anemometer measurement and the error in our model, a tunnel air velocity error of 15% was applied in the calculation of emission rate error (Appendix A).

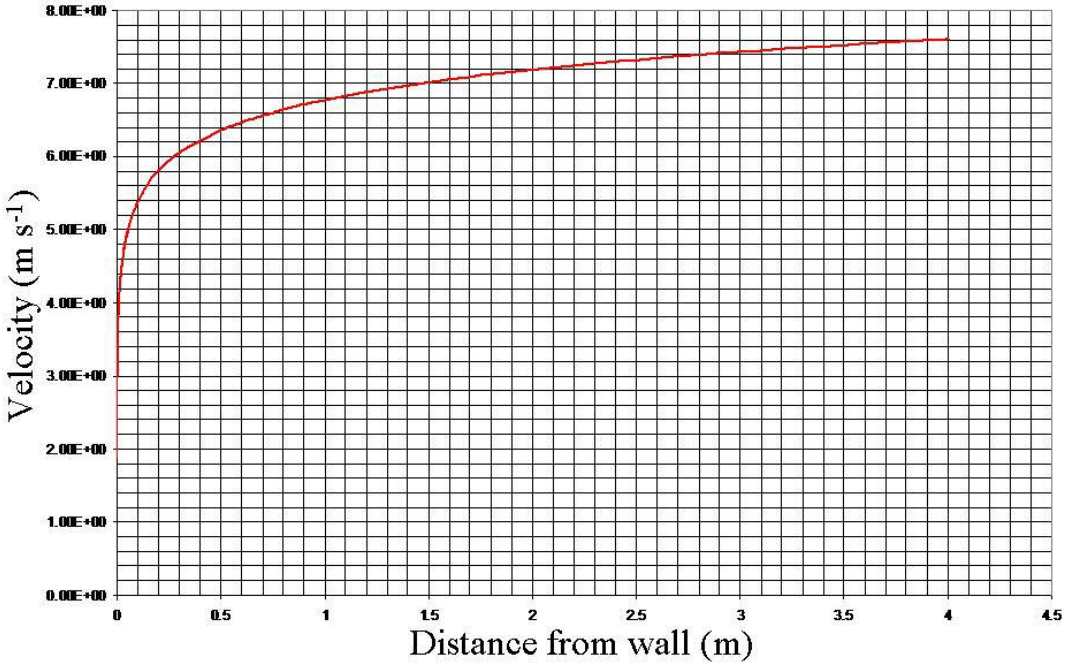
Tables

Table B.1 Measured velocity and calculated mean velocity from velocity profile for turbulent flow for both tunnel entrance and exit on five different sampling dates in the Fort McHenry Tunnel, Baltimore, Maryland.

Sampling Date	Measured Velocity at Entrance Exhaust ($m\ s^{-1}$)	Mean Velocity from Model ($m\ s^{-1}$)	Correction Factor	Measured Velocity at Exit Exhaust ($m\ s^{-1}$)	Mean Velocity from Model ($m\ s^{-1}$)	Correction Factor
29 Jul 2003	N/A	N/A	N/A	5.94	6.2	4%
29 Sep 2003	4.47	4.8	7%	5.14	5.4	5%
14 Nov 2003	5.17	5.5	6%	6.45	6.7	4%
22 Mar 2004	4.92	5.2	6%	5.78	6.0	4%
10 Jun 2004	5.45	5.7	5%	6.23	6.5	4%
	Average Entrance Correction Factor >>		6.0%	**Average Exit Correction Factor >>**		4.3%

Figures

Figure B.1 Tunnel velocity profile calculated using model from Perry's Chemical Engineers' Handbook (Green and Maloney, 1997) for a mean tunnel velocity of 6.2 m s^{-1}.



Literature Cited

(1) Allen, J.O.; Mayo, P.R.; Hughes, L.S.; Salmon, L.G.; Cass, G.R. Emissions of Size-Segregated Aerosols from On-Road Vehicles in the Caldecott Tunnel. *Environmental Science and Technology.* 2001, *35*, 4189-4197.

(2) Andersen, H.V.; Hovmand, M.F. Measurements of Ammonia and Ammonium by Denuder and Filter Pack. *Atmospheric Environment.* 1994, *28*, 3495-3512.

(3) Battye, R.; Battye, W.; Overcash, C.; Fudge, S. Development and Selection of Ammonia Emission Factors. Prepared by EC/R, Inc. for the US-EPA Atmospheric Research and Exposure Assessment Laboratory. 1994.

(4) Baum, M.M.; Kiyomiya, E.S.; Kumar, S.; Lappas, A.M. Multicomponent Remote Sensing of Vehicle Exhaust by Dispersive Absorption Spectroscopy. 2. Direct On-Road Ammonia Measurements. *Environmental Science and Technology*. 2001, *35*, 3735-3741.

(5) Cadle, S.H.; Mulawa, P.A. Low Molecular Weight Aliphatic Amines in Exhaust from Catalyst-Equipped Cars. *Environmental Science and Technology*. 1980, *14*, 718-723.

(6) Castro, M.S.; Driscoll, C.T. Atmospheric Nitrogen Deposition to Estuaries in the Mid-Atlantic and Northeastern United States. *Environmental Science and Technology*. 2002, *36*, 3242-3249.

(7) Chen, L.-W.A.; Chow, J.C.; Doddridge, B.G.; Dickerson, R.R.; Ryan, W.F.; Mueller, P.K. Analysis of a Summertime PM2.5 and Haze Episode in the

Mid-Atlantic Region. *Journal of the Air and Waste Management Association*. 2003, *53*, 946-956.

(8) Chinkin, L.R.; Ryan, P.A.; Coe, D.L. Recommended Improvements to the CMU Ammonia Emission Inventory Model for Use by LADCO. Prepared by Sonoma Technology, Inc. for the Lake Michigan Air Directors Consortium. 2003.

(9) Churg, A.; Brauer, M. Ambient Atmospheric Particles in the Airways of Human Lungs. *Ultrastructural Pathology*. 2000, *24*, 353-361.

(10) Davidson, C.; Strader, R; Anderson, N.; Goebes, M.; Ayers, J. Development of an Improved Ammonia Emissions Inventory for the United States. Prepared for the Northeast States for Coordinated Air Use Management (NESCAUM) and the Mid-Atlantic Regional Air Management Association (MARAMA). 2001.

(11) Der, K.; Jannejohn, D.; Mignacca, D.; Sidi, S.; Visser, R. Ammonia Emission Inventory for the Lower Fraser Valley Airshed. Prepared by the Greater Vancouver Regional District Air Quality Department. 1999.

(12) Dockery, D.W.; Pope, C.A.; Xu, X.; Spengler, J.D.; Ware, J.H.; Fay, M.E.; Ferris, B.G.; Speizer, F.E. An Association Between Air Pollution and Mortality in Six U.S. Cities. *The New England Journal of Medicine*. 1993, *329*, 1753-1759.

(13) Durbin, T.D.; Wilson, R.D.; Norbeck, J.M.; Miller, J.W.; Huai, T.; Rhee, S.H. Estimates of the Emission Rates of Ammonia From Light-Duty Vehicles

Using Standard Chassis Dynamometer Test Cycles. *Atmospheric Environment*. 2002, *36*, 1475-1482.

(14) Fraser, M.P.; Cass, G.R. Detection of Excess Ammonia Emissions from In-Use Vehicles and the Implications for Fine Particle Control. *Environmental Science and Technology*. 1998, *32*, 1053-1057.

(15) *Perry's Chemical Engineers' Handbook*; Editor, Green, D.W.; Editor, Maloney, J.O. 7th ed. McGraw Hill: New York, NY, 1997.

(16) Howarth, R.W.; Billen, G.; Swaney, D.; Townsend, A.; Jaworski, N.; Lajtha, K.; Downing, J.A.; Elmgren, R.; Caraco, N.; Jordan, R.; Berendse, F.; Freney, J.; Kudeyarov, V.; Murdoch, P.; Shao-Liang, Z. Regional Nitrogen Budgets and Riverine N & P Fluxes for the Drainages to the North Atlantic Ocean: Natural and Human Influences. *Biogeochemistry*. 1996, *35*, 75.

(17) Huai, T.; Durbin, T.D.; Miller, J.W.; Pisano, J.T.; Sauer, C.G.; Rhee, S.H.; Norbeck, J.M. Investigation of NH_3 Emissions from New Technology Vehicles as a Function of Vehicle Operating Conditions. *Environmental Science and Technology*. 2000, *37*, 4841-4847.

(18) Hughes, L.S.; Allen, J.O.; Salmon, L.G.; Mayo, P.R.; Johnson, R.J.; Cass, G.R. Evolution of Nitrogen Species Air Pollutants Along Trajectories Crossing the Los Angeles Area. *Environmental Science and Technology*. 2002, *36*, 3928-3935.

(19) Kean, A.J.; Harley, R.A.; Littlejohn, D.; Kendall, G.R. On-road Measurement of Ammonia and Other Motor Vehicle Exhaust Emissions. *Environmental Science and Technology*. 2000, *34*, 3535-3539.

(20) Landis, M.S.; Norris, G.A.; Williams, R.W.; Weinstein, J.P. Personal Exposures to PM2.5 Mass and Trace Elements in Baltimore, MD, USA. *Atmospheric Environment*. 2001, *35*, 6511-6524.

(21) Li, J.; Dasgupta, P.K.; Genfa, Z. Transversely Illuminated Liquid Core Waveguide Based Fluorescence Detection. Fluorometric Flow Injection Determination of Aqueous Ammonium/Ammonia. *Talanta*. 1999, *50*, 617-623.

(22) Maryland Department of Transportation (MDOT), 2003. *Millions of Annual Vehicle Miles Report*.

(23) Moeckli, M.A.; Fierz, M.; Sigrist, M.W. Emission Factors for Ethane and Ammonia from a Tunnel Study with a Photoacoustic Trace Gas Detection System. *Environmental Science and Technology*. 1996, *30*, 2864-2867.

(24) Ott, R.L.; Longnecker, M. *An Introduction to Statistical Methods and Data Analysis*; 5th ed. Wadsworth Group: Pacific Grove, CA, 2001.

(25) Pierson, W.R.; Brachaczek, W.W. Emissions of Ammonia and Amines from Vehicles on the Road. *Environmental Science and Technology*. 1983, *17*, 757-760.

(26) Pierson, W.R.; Gertler A.W.; Robinson N.F.; Sagebiel J.C.; Zielinska B.; Bishop, G.A.; Stedman, D.H.; Zweidinger, R.B.; Ray, W.D. Real-world Automotive Emissions – Summary of Studies in the Fort McHenry and Tuscarora Mountain Tunnels. *Atmospheric Environment*. 1996, *30*, 2233-2256.

(27) Pisano, J.T.; Fitz, D.R. *Flux Measurements of Ammonia to Estimate Emission Factors for Area Sources.* Final Report to California Air Resources Board under Contract 98-340. CE-CERT document 02-AP-18395-004-FR. 2002.

(28) Roadman, M.J., Scudlark, J.R., Meisinger, J.J., Ullman, W.J. Validation of Ogawa Passive Samplers for the Determination of Gaseous Ammonia Concentrations in Agricultural Settings. *Atmospheric Environment*. 2003, *37*, 2317-2325.

(29) Siefert, R.L.; Scudlark, J.R.; Potter, A.G.; Simonsen, K.A.; Savidge, K.B. Characterization of Atmospheric Ammonia Emissions from a Commercial Chicken House on the Delmarva Peninsula. *Environmental Science and Technology*. 2004, *38*, 2769-2778.

(30) Skoog, D.A. Principles of Instrumental Analysis; 3rd ed. Saunders College Publishing: Philadelphia, PA, 1985.

(31) Technicon Industrial Systems. *Technicon Industrial Method No. 804-86T*. Tarrytown, New York, 1986.

(32) U.S. Environmental Protection Agency, Center for Environmental Research Information, Office of Research and Development. *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air.* Document EPA/625/R-96/010a. Washington, D.C., 1999.